(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 May 2007 (03.05.2007)

PCT

(10) International Publication Number
WO 2007/051078 A2

(51) International Patent Classification:
G06F 19/00 (2006.01)

(21) International Application Number:
PCT/US2006/042692

(22) International Filing Date: 30 October 2006 (30.10.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/730,882	28 October 2005 (28.10.2005)	US
60/732,154	2 November 2005 (02.11.2005)	US
60/737,744	18 November 2005 (18.11.2005)	US
60/758,528	13 January 2006 (13.01.2006)	US
60/780,518	9 March 2006 (09.03.2006)	US
60/788,694	4 April 2006 (04.04.2006)	US
60/812,590	12 June 2006 (12.06.2006)	US
60/815,253	21 June 2006 (21.06.2006)	US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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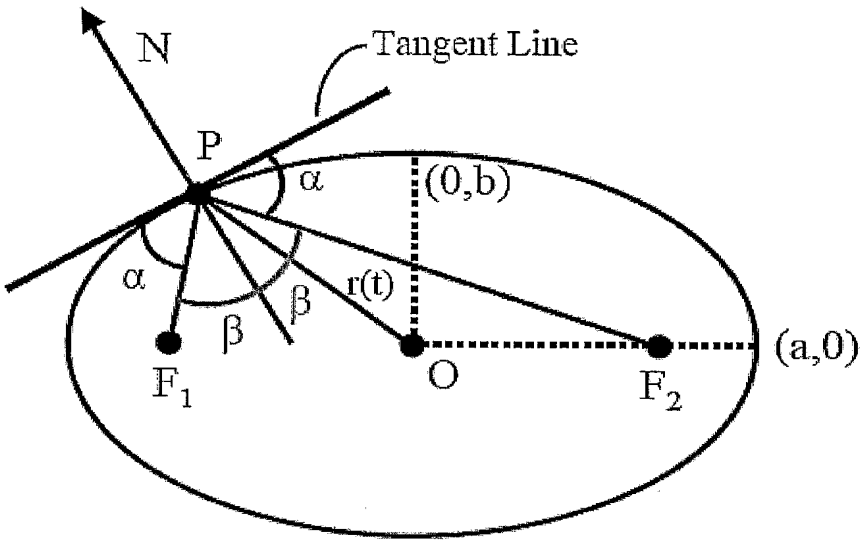
(54) Title: SYSTEM AND METHOD OF COMPUTING AND RENDERING THE NATURE OF POLYATOMIC MOLECULES AND POLYATOMIC MOLECULAR IONS



(57) Abstract: A method and system of physically solving the charge, mass, and current density functions of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species using Maxwell's equations and computing and rendering the physical nature of the chemical bond using the solutions. The results can be displayed on visual or graphical media. The display can be static or dynamic such that electron motion and specie's vibrational, rotational, and translational motion can be displayed in an embodiment. The displayed information is useful to anticipate reactivity and physical properties. The insight into the nature of the chemical bond of at least one specie can permit the solution and display of those of other species to provide utility to anticipate their reactivity and physical properties.

WO 2007/051078 A2

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SYSTEM AND METHOD OF COMPUTING AND RENDERING THE NATURE OF POLYATOMIC MOLECULES AND POLYATOMIC MOLECULAR IONS

This application claims priority to U.S. Application Nos.: 60/730,882, filed October 28, 2005; 60/732,154, filed November 2, 2005; 60/737,744, filed November 18, 2005; 60/758,528, filed January 13, 2006; 60/780,518, filed March 9, 2006; 60/788,694, filed April 4, 2006; 60/812,590, filed June 12, 2006; and 60/815,253, June 21, 2006, the complete disclosures of which are incorporated herein by reference.

Field of the Invention:

This invention relates to a system and method of physically solving the charge, mass, and current density functions of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species, and computing and rendering the nature of these species using the solutions. The results can be displayed on visual or graphical media. The displayed information provides insight into the nature of these species and is useful to anticipate their reactivity, physical properties, and spectral absorption and emission, and permits the solution and display of other species.

Rather than using postulated unverifiable theories that treat atomic particles as if they were not real, physical laws are now applied to atoms and ions. In an attempt to provide some physical insight into atomic problems and starting with the same essential physics as Bohr of the e^- moving in the Coulombic field of the proton with a true wave equation, as opposed to the diffusion equation of Schrödinger, a classical approach is explored which yields a model that is remarkably accurate and provides insight into physics on the atomic level. The proverbial view deeply seated in the wave-particle duality notion that there is no large-scale physical counterpart to the nature of the electron is shown not to be correct. Physical laws and intuition may be restored when dealing with the wave equation and quantum atomic problems.

Specifically, a theory of classical quantum mechanics (CQM) was derived from first principles as reported previously [reference Nos. 1-8] that successfully applies physical laws to the solution of atomic problems that has its basis in a breakthrough in the understanding of the stability of the bound electron to radiation. Rather than using the postulated Schrödinger boundary condition: "$\Psi \to 0$ as $r \to \infty$", which leads to a purely mathematical model of the electron, the constraint is based on experimental observation. Using Maxwell's equations, *the*

classical wave equation is solved with the constraint that the bound $n = 1$-state electron cannot radiate energy. Although it is well known that an accelerated *point* particle radiates, an *extended distribution* modeled as a superposition of accelerating charges does not have to radiate. A simple invariant physical model arises naturally wherein the predicted results are extremely straightforward and internally consistent requiring minimal math, as in the case of the most famous equations of Newton, Maxwell, Einstein, de Broglie, and Planck on which the model is based. No new physics is needed; only the known physical laws based on direct observation are used.

Applicant's previously filed WO2005/067678 discloses a method and system of physically solving the charge, mass, and current density functions of atoms and atomic ions and computing and rendering the nature of these species using the solutions. The complete disclosure of this published PCT application is incorporated herein by reference.

Applicant's previously filed WO2005/116630 discloses a method and system of physically solving the charge, mass, and current density functions of excited states of atoms and atomic ions and computing and rendering the nature of these species using the solutions. The complete disclosure of this published PCT application is incorporated herein by reference.

Applicant's previously filed U.S. Published Patent Application No. 20050209788A1, relates to a method and system of physically solving the charge, mass, and current density functions of hydrogen-type molecules and molecular ions and computing and rendering the nature of the chemical bond using the solutions. The complete disclosure of this published application is incorporated herein by reference.

Background of the Invention

The old view that the electron is a zero or one-dimensional point in an all-space probability wave function $\Psi(x)$ is not taken for granted. The theory of classical quantum mechanics (CQM), derived from first principles, must successfully and consistently apply physical laws on all scales [1-8]. Stability to radiation was ignored by all past atomic models. Historically, the point at which QM broke with classical laws can be traced to the issue of nonradiation of the one electron atom. Bohr just postulated orbits stable to radiation with the further postulate that the bound electron of the hydrogen atom does not obey Maxwell's equations—rather it obeys different physics [1-12]. Later physics was replaced by "pure mathematics" based on the notion of the inexplicable wave-particle duality nature of electrons

which lead to the Schrödinger equation wherein the consequences of radiation predicted by Maxwell's equations were ignored. Ironically, Bohr, Schrödinger, and Dirac used the Coulomb potential, and Dirac used the vector potential of Maxwell's equations. But, all ignored electrodynamics and the corresponding radiative consequences. Dirac originally attempted to solve the bound electron physically with stability with respect to radiation according to Maxwell's equations with the further constraints that it was relativistically invariant and gave rise to electron spin [13]. He and many founders of QM such as Sommerfeld, Bohm, and Weinstein wrongly pursued a planetary model, were unsuccessful, and resorted to the current mathematical-probability-wave model that has many problems [9-16]. Consequently, Feynman for example, attempted to use first principles including Maxwell's equations to discover new physics to replace quantum mechanics [17].

Physical laws may indeed be the root of the observations thought to be "purely quantum mechanical", and it was a mistake to make the assumption that Maxwell's electrodynamic equations must be rejected at the atomic level. Thus, in the present approach, the classical wave equation is solved with the constraint that a bound $n = 1$-state electron cannot radiate energy.

Herein, derivations consider the electrodynamic effects of moving charges as well as the Coulomb potential, and the search is for a solution representative of the electron wherein there is acceleration of charge motion without radiation. The mathematical formulation for zero radiation based on Maxwell's equations follows from a derivation by Haus [18]. The function that describes the motion of the electron must not possess spacetime Fourier components that are synchronous with waves traveling at the speed of light. Similarly, nonradiation is demonstrated based on the electron's electromagnetic fields and the Poynting power vector.

It was shown previously [1-8] that CQM gives closed form solutions for the atom including the stability of the $n = 1$ state and the instability of the excited states, the equation of the photon and electron in excited states, and the equation of the free electron and photon, which predict the wave particle duality behavior of particles and light. The current and charge density functions of the electron may be directly physically interpreted. For example, spin angular momentum results from the motion of negatively charged mass moving systematically, and the equation for angular momentum, $\mathbf{r} \times \mathbf{p}$, can be applied directly to the wave function (a current density function) that describes the electron. The magnetic moment of a Bohr magneton, Stern Gerlach experiment, g factor, Lamb shift, resonant line width and

shape, selection rules, correspondence principle, wave particle duality, excited states, reduced mass, rotational energies, and momenta, orbital and spin splitting, spin-orbital coupling, Knight shift, and spin-nuclear coupling, and elastic electron scattering from helium atoms, are derived in closed-form equations based on Maxwell's equations. The calculations agree with experimental observations.

The Schrödinger equation gives a vague and fluid model of the electron. Schrödinger interpreted $e\Psi^*(x)\Psi(x)$ as the charge-density or the amount of charge between x and $x+dx$ (Ψ^* is the complex conjugate of Ψ). Presumably, then, he pictured the electron to be spread over large regions of space. After Schrödinger's interpretation, Max Born, who was working with scattering theory, found that this interpretation led to inconsistencies, and he replaced the Schrödinger interpretation with the probability of finding the electron between x and $x+dx$ as

$$\int \Psi(x)\Psi^*(x)\,dx \qquad (1)$$

Born's interpretation is generally accepted. Nonetheless, interpretation of the wave function is a never-ending source of confusion and conflict. Many scientists have solved this problem by conveniently adopting the Schrödinger interpretation for some problems and the Born interpretation for others. This duality allows the electron to be everywhere at one time—yet have no volume. Alternatively, the electron can be viewed as a discrete particle that moves here and there (from $r=0$ to $r=\infty$), and $\Psi\Psi^*$ gives the time average of this motion.

In contrast to the failure of the Bohr theory and the nonphysical, adjustable-parameter approach of quantum mechanics, multielectron atoms [1, 4] and the nature of the chemical bond [1, 5] are given by exact closed-form solutions containing fundamental constants only. Using the nonradiative wave equation solutions that describe the bound electron having conserved momentum and energy, the radii are determined from the force balance of the electric, magnetic, and centrifugal forces that corresponds to the minimum of energy of the system. The ionization energies are then given by the electric and magnetic energies at these radii. The spreadsheets to calculate the energies from exact solutions of one through twenty-electron atoms are given in '06 Mills GUT [1] and are available from the internet [19]. For 400 atoms and ions, as well as hundreds of molecules, the agreement between the predicted and experimental results is remarkable.

The background theory of classical quantum mechanics (CQM) for the physical solutions of atoms and atomic ions is disclosed in R. Mills, *The Grand Unified Theory of*

Classical Quantum Mechanics, January 2000 Edition, BlackLight Power, Inc., Cranbury, New Jersey, (" '00 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512; R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, September 2001 Edition, BlackLight Power, Inc., Cranbury, New Jersey, Distributed by Amazon.com (" '01 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512; R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, July 2004 Edition, BlackLight Power, Inc., Cranbury, New Jersey, (" '04 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512; R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, January 2005 Edition, BlackLight Power, Inc., Cranbury, New Jersey, (" '05 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512 (posted at www.blacklightpower.com); R. L. Mills, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834, (" '06 Mills GUT"), provided by BlackLight Power, Inc., 493 Old Trenton Road, Cranbury, NJ, 08512 (posted at http://www.blacklightpower.com/bookdownload.shtml); in prior PCT applications PCT/US02/35872; PCT/US02/06945; PCT/US02/06955; PCT/US01/09055; PCT/US01/25954; PCT/US00/20820; PCT/US00/20819; PCT/US00/09055; PCT/US99/17171; PCT/US99/17129; PCT/US 98/22822; PCT/US98/14029; PCT/US96/07949; PCT/US94/02219; PCT/US91/08496; PCT/US90/01998; and PCT/US89/05037 and U.S. Patent No. 6,024,935; the entire disclosures of which are all incorporated herein by reference (hereinafter "Mills Prior Publications").

The following list of references, which are also incorporated herein by reference in their entirety, are referred to in the above sections using [brackets]:

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2. R. L. Mills, "Classical Quantum Mechanics", Physics Essays, Vol. 16, No. 4, December, (2003), pp. 433-498; posted with spreadsheets at www.blacklightpower.com/techpapers.shtml.

3. R. Mills, "Physical Solutions of the Nature of the Atom, Photon, and Their Interactions to Form Excited and Predicted Hydrino States", submitted.
4. R. L. Mills, "Exact Classical Quantum Mechanical Solutions for One- Through Twenty-Electron Atoms", in press, posted with spreadsheets at http://www.blacklightpower.com/techpapers.shtml.
5. R. L. Mills, "The Nature of the Chemical Bond Revisited and an Alternative Maxwellian Approach", Physics Essays, Vol. 17, (2004), pp. 342-389, posted with spreadsheets at http://www.blacklightpower.com/techpapers.shtml.
6. R. L. Mills, "Maxwell's Equations and QED: Which is Fact and Which is Fiction", in press, posted with spreadsheets at http://www.blacklightpower.com/techpapers.shtml.
7. R. L. Mills, "Exact Classical Quantum Mechanical Solution for Atomic Helium Which Predicts Conjugate Parameters from a Unique Solution for the First Time", submitted, posted with spreadsheets at http://www.blacklightpower.com/theory/theory.shtml..
8. R. Mills, "The Grand Unified Theory of Classical Quantum Mechanics", Int. J. Hydrogen Energy, Vol. 27, No. 5, (2002), pp. 565-590.
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209-211.

18. Haus, H. A., "On the radiation from point charges", American Journal of Physics, 54, (1986), pp. 1126-1129.

19. http://www.blacklightpower.com/new.shtml.

SUMMARY OF THE INVENTION

The present invention, an exemplary embodiment of which is also referred to as Millsian software, stems from a new fundamental insight into the nature of the atom. Applicant's new theory of Classical Quantum Mechanics (CQM) reveals the nature of atoms and molecules using classical physical laws for the first time. As discussed above, traditional quantum mechanics can solve neither multi-electron atoms nor molecules exactly. By contrast, CQM produces exact, closed-form solutions containing physical constants only for even the most complex atoms and molecules.

The present invention is the first and only molecular modeling program ever built on the CQM framework. All the major functional groups that make up most organic molecules have been solved exactly in closed-form solutions with CQM. By using these functional groups as building blocks, or independent units, a potentially infinite number of organic molecules can be solved. As a result, the present invention can be used to visualize the exact 3D structure and calculate the heat of formation of almost any organic molecule.

For the first time, the significant building-block molecules of chemistry have been successfully solved using classical physical laws in exact closed-form equations having fundamental constants only. The major functional groups have been solved from which molecules of infinite length can be solved almost instantly with a computer program. The predictions are accurate within experimental error for over 375 exemplary molecules.

Applicant's CQM is the theory that physical laws (Maxwell's Equations, Newton's Laws, Special and General Relativity) must hold on all scales. The theory is based on an often overlooked result of Maxwell's Equations, that an extended distribution of charge may, under certain conditions, accelerate without radiating. This "condition of no radiation" is invoked to solve the physical structure of subatomic particles, atoms, and molecules.

In exact closed-form equations with physical constants only, solutions to thousands of known experimental values arise that were beyond the reach of previous outdated theories. These include the electron spin, g-factor, multi-electron atoms, excited states, polyatomic molecules, wave-particle duality and the nature of the photon, the masses and families of

fundamental particles, and the relationships between fundamental laws of the universe that reveal why the universe is accelerating as it expands. CQM is successful to over 85 orders of magnitude, from the level of quarks to the cosmos. Applicant now has over 65 peer-reviewed journal articles and also books discussing the CQM and supporting experimental evidence.

The molecular modeling market was estimated to be a two-billion-dollar per year industry in 2002, with hundreds of millions of government and industry dollars invested in computer algorithms and supercomputer centers. This makes it the largest effort of computational chemistry and physics.

The present invention's advantages over other models includes: Rendering true molecular structures; Providing precisely all characteristics, spatial and temporal charge distributions and energies of every electron in every bond, and of every bonding atom; Facilitating the identification of biologically active sites in drugs; and Facilitating drug design.

An objective of the present invention is to solve the charge (mass) and current-density functions of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species from first principles. In an embodiment, the solution for the polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species is derived from Maxwell's equations invoking the constraint that the bound electron before excitation does not radiate even though it undergoes acceleration.

Another objective of the present invention is to generate a readout, display, or image of the solutions so that the nature of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species be better understood and potentially applied to predict reactivity and physical and optical properties.

Another objective of the present invention is to apply the methods and systems of solving the nature of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species and their rendering to numerical or graphical form to all atoms and atomic ions.

These objectives and other objectives are obtained by a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising

physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

Also provided is a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles,charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

The presented exact physical solutions for known species of the group of polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any functional group therein, can be applied to other species. These solutions can be used to predict the properties of other species and engineer compositions of matter in a manner which is not possible using past quantum mechanical techniques. The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. Not only can new stable compositions of matter be predicted, but now the structures of combinatorial chemistry reactions can be predicted.

Pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the specie to be identified from the common spatial charge-density functions of a series of active species. Novel drugs can now be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.

The system can be used to calculate conformations, folding, and physical properties, and the exact solutions of the charge distributions in any given specie are used to calculate the fields. From the fields, the interactions between groups of the same specie or between groups on different species are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

Embodiments of the system for performing computing and rendering of the nature of the polyatomic molecules, polyatomic molecular ions, diatomic molecules, molecular radicals, molecular ions, or any portion of these species using the physical solutions may comprise a general purpose computer. Such a general purpose computer may have any number of basic configurations. For example, such a general purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input means, such as a keyboard or mouse, a display device, and a printer or other output device. A system implementing the present invention can also comprise a special purpose computer or other hardware system and all should be included within its scope.

Although not preferred, any of the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an elliptical current element of the prolate spheroidal MO;

Fig. 2 illustrates the ellipsoidal current-density surface obtained by stretching $Y_0^0(\theta,\phi)$ along the semimajor axis;

Fig. 3 illustrates the angular momentum components of the MO and $\mathbf{S}$;

Fig. 4 illustrates cross section of an atomic orbital;

Fig. 5 illustrates **A**. Prolate spheroid MO;

Fig. 6 illustrates the equilateral triangular $H_3^+(1/p)$;

Fig. 7 illustrates the cross section of the OH MO;

Fig. 8 illustrates OH MO comprising the superposition of the H_2-type ellipsoidal MO and the $O2p_y$ AO with a relative charge-density of 0.75 to 1.25;

Fig. 9 illustrates H_2O MO comprising the linear combination of two $O-H$ -bond MOs;

Fig. 10 illustrates the cross section of the NH MO showing the axes, angles, and point of intersection of the H_2-type ellipsoidal MO with the $N2p_x$ AO;

Fig. 11 illustrates NH MO comprising the superposition of the H_2-type ellipsoidal MO and the $N2p_x$ AO with a relative charge-density of 0.75 to 1.25;

Fig. 12 illustrates NH_2 MO comprising the linear combination of two $N-H$ -bond MOs;

Fig. 13 illustrates NH_3 MO comprising the linear combination of three $N-H$ -bonds;

Fig. 14 illustrates the cross section of the CH MO showing the axes, angles, and point of intersection of the H_2 -type ellipsoidal MO with the $C2sp^3$ HO;

Fig. 15 illustrates CH MO comprising the superposition of the H_2 -type ellipsoidal MO and the $C2sp^3$ HO with a relative charge-density of 0.75 to 1.25;

Fig. 16 illustrates CH_2 MO comprising the linear combination of two $C-H$ -bond MOs;

Fig. 17 illustrates CH_3 MO comprising the linear combination of three $C-H$ -bond MOs;

Fig. 18 illustrates CH_4 MO comprising the linear combination of four $C-H$ -bond MOs formed by the superposition of a H_2 -type ellipsoidal MO and a $C2sp^3$ HO;

Fig. 19 illustrates the cross section of the N_2 MO;

Fig. 20 illustrates N_2 MO comprising the σ MO (H_2 -type MO) with N atoms at the foci;

Fig. 21 illustrates the cross section of the O_2 MO;

Fig. 22 illustrates O_2 MO comprising the σ MO (H_2 -type MO);

Fig. 23 illustrates the cross section of the F_2 MO;

Fig. 24 illustrates F_2 MO comprising the σ MO (H_2 -type MO) with F atoms at the foci;

Fig. 25 illustrates the cross section of the Cl_2 MO;

Fig. 26 illustrates Cl_2 MO comprising the superposition of the H_2 -type ellipsoidal MO and the two $Cl3sp^3$ HOs;

Fig. 27 illustrates the cross section of the CN MO;

Fig. 28 illustrates CN MO;

Fig. 29 illustrates the cross section of the CO MO;

Fig. 30 illustrates CO MO;

Fig. 31 illustrates the cross section of the NO MO;

Fig. 32 illustrates NO MO;

Fig. 33 illustrates the cross section of the CO_2 MO;

Fig. 34 illustrates CO_2 MO;

Fig. 35 illustrates the cross section of the NO_2 MO;

Fig. 36 illustrates NO_2 MO;

Fig. 37 illustrates the cross section of the $C-C$ -bond MO (σ MO) and one $C-H$ -bond

MO of ethane;

Fig. 38 illustrates the cross section of one $C-H$-bond MO of ethane showing the axes, angles, and point of intersection of the H_2-type ellipsoidal MO with the $C_{ethane}2sp^3$ HO;

Fig. 39 illustrates CH_3CH_3 MO comprising the linear combination of two sets of three $C-H$-bond MOs and a $C-C$-bond MO;

Fig. 40 illustrates the cross section of the $C=C$-bond MO (σ MO) and one $C-H$-bond MO of ethylene showing the axes, angles, and point of intersection of each H_2-type ellipsoidal MO with the corresponding $C_{ethylene}2sp^3$ HO;

Fig. 41 illustrates the cross section of one $C-H$-bond MO of ethylene showing the axes, angles, and point of intersection of the H_2-type ellipsoidal MO with the $C_{ethylene}2sp^3$ HO;

Fig. 42 illustrates CH_2CH_2 MO comprising the linear combination of two sets of two $C-H$-bond MOs and a $C=C$-bond MO;

Fig. 43 illustrates the cross section of the $C\equiv C$-bond MO (σ MO) and one $C-H$-bond MO of acetylene showing the axes, angles, and point of intersection of each H_2-type ellipsoidal MO with the corresponding $C_{acetylene}2sp^3$ HO;

Fig. 44 illustrates $CHCH$ MO comprising the linear combination of two $C-H$-bond MOs and a $C\equiv C$-bond MO;

Fig. 45 illustrates the cross section of one $C=C$-bond MO (σ MO) and one $C-H$-bond MO of benzene showing the axes, angles, and point of intersection of each H_2-type ellipsoidal MO with the corresponding $C_{benzene}2sp^3$ HO;

Fig. 46 illustrates the cross section of one $C-H$-bond MO of benzene showing the axes, angles, and point of intersection of the H_2-type ellipsoidal MO with the $C_{benzene}2sp^3$ HO;

Fig. 47 illustrates C_6H_6 MO comprising the linear combination of six sets of $C-H$-bond MOs bridged by $C=C$-bond MOs;

Fig. 48 illustrates the cross section of one $C-C$-bond MO (σ MO) and one $C-H$-bond MO of C_nH_{2n+2} showing the axes, angles, and point of intersection of each H_2-type ellipsoidal MO with the corresponding $C_{alkane}2sp^3$ HO;

Fig. 49 illustrates the cross section of one $C-H$-bond MO of C_nH_{2n+2} showing the axes, angles, and point of intersection of the H_2-type ellipsoidal MO with the $C_{alkane}2sp^3$ HO;

Fig. 50 illustrates C_3H_8 MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl groups and one methylene group;

Fig. 51 illustrates C_4H_{10} MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and two methylene groups;

Fig. 52 illustrates C_5H_{12} MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and three methylene groups;

Fig. 53 illustrates C_6H_{14} MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and four methylene groups;

Fig. 54 illustrates C_7H_{16} MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and five methylene groups;

Fig. 55 illustrates C_8H_{18} MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and six methylene groups;

Fig. 56 illustrates C_9H_{20} MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and seven methylene groups. (A) Opaque view of the charge-density of the $C-C$-bond and $C-H$-bond MOs;

Fig. 57 illustrates $C_{10}H_{22}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and eight methylene groups;

Fig. 58 illustrates $C_{11}H_{24}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and nine methylene groups;

Fig. 59 illustrates $C_{12}H_{26}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and ten methylene groups;

Fig. 60 illustrates $C_{18}H_{38}$ MO comprising a linear combination of $C-H$-bond MOs and $C-C$-bond MOs of the two methyl and sixteen methylene groups;

Fig. 61.A illustrates 1,3 Butadiene;

Fig. 61.B illustrates 1,3 Pentadiene;

Fig. 61.C illustrates 1,4 Pentadiene;

Fig. 61.D illustrates 1,3 Cyclopentadiene;

Fig. 61E illustrates Cyclopentene;

Fig. 62 illustrates Naphthalene;

Fig. 63 illustrates Toluene;

Fig. 64 illustrates Benzoic acid;

Fig. 65 illustrates Pyrrole;

Fig. 66 illustrates Furan;

Fig. 67 illustrates Thiophene;

Fig. 68 illustrates Imidazole;

Fig. 69 illustrates Pyridine;

Fig. 70 illustrates Pyrimidine;

Fig. 71 illustrates Pyrazine;

Fig. 72 illustrates Quinoline;

Fig. 73 illustrates Isoquinoline;

Fig. 74 illustrates Indole;

Fig. 75 illustrates Adenine;

Fig. 76 illustrates a block diagram of an exemplary software program; and

Figs. 77 and 78 illustrate pictures of an exemplary software program.

Section I

THE NATURE OF THE CHEMICAL BOND OF HYDROGEN-TYPE MOLECULES AND MOLECULAR IONS

With regard to the Hydrino Theory—BlackLight Process section, the possibility of states with $n=1/p$ is also predicted in the case of hydrogen molecular species wherein $H(1/p)$ reacts a proton or two $H(1/p)$ atoms react to form $H_2^+(1/p)$ and $H_2(1/p)$, respectively. The natural molecular-hydrogen coordinate system based on symmetry is ellipsoidal coordinates. The magnitude of the central field in the derivations of molecular hydrogen species is taken as the general parameter p wherein p may be an integer which may be predictive of new possibilities. Thus, p replaces the effective nuclear charge of quantum mechanics and corresponds to the physical field of a resonant photon superimposed with the field of the proton. The case with $p=1$ is evaluated and compared with the experimental results for hydrogen species in Table 11.1, and the consequences that $p=$ integer are considered in the Nuclear Magnetic Resonance Shift section.

Two hydrogen atoms react to form a diatomic molecule, the hydrogen molecule.

$$2H\left[a_H\right]\rightarrow H_2\left[2c'=\sqrt{2}a_o\right] \tag{11.1}$$

where $2c'$ is the internuclear distance. Also, two hydrino atoms react to form a diatomic molecule, a dihydrino molecule.

$$2H\left[\frac{a_H}{p}\right]\rightarrow H_2\left[2c'=\frac{\sqrt{2}a_o}{p}\right] \tag{11.2}$$

where p is an integer.

Hydrogen molecules form hydrogen molecular ions when they are singly ionized.

$$H_2\left[2c'=\sqrt{2}a_o\right]\rightarrow H_2\left[2c'=2a_o\right]^+ + e- \tag{11.3}$$

Also, dihydrino molecules form dihydrino molecular ions when they are singly ionized.

$$H_2\left[2c'=\frac{\sqrt{2}a_o}{p}\right]\rightarrow H_2\left[2c'=\frac{2a_o}{p}\right]^+ + e- \tag{11.4}$$

HYDROGEN-TYPE MOLECULAR IONS

Each hydrogen-type molecular ion comprises two protons and an electron where the equation of motion of the electron is determined by the central field which is p times that of a proton at each focus (p is one for the hydrogen molecular ion, and p is an integer greater than one for each $H_2^+(1/p)$, called dihydrino molecular ion). The differential equations of motion in the case of a central field are [1]

$$m(\ddot{r} - r\dot{\theta}^2) = f(r) \tag{11.5}$$

$$m(2\dot{r}\dot{\theta} + r\ddot{\theta}) = 0 \tag{11.6}$$

The second or transverse equation, Eq. (11.6), gives the result that the angular momentum is constant.

$$r^2\dot{\theta} = \text{constant} = L/m \tag{11.7}$$

where L is the angular momentum ($\hbar$ in the case of the electron). The central force equations can be transformed into an orbital equation by the substitution, $u = \frac{1}{r}$. The differential equation of the orbit of a particle moving under a central force is

$$\frac{\partial^2 u}{\partial \theta^2} + u = \frac{-1}{\frac{mL^2u^2}{m^2}} f(u^{-1}) \tag{11.8}$$

Because the angular momentum is constant, motion in only one plane need be considered; thus, the orbital equation is given in polar coordinates. The solution of Eq. (11.8) for an inverse-squared force

$$f(r) = -\frac{k}{r^2} \tag{11.9}$$

is

$$r = r_0 \frac{1+e}{1+e\cos\theta} \tag{11.10}$$

$$e = A\frac{m\frac{L^2}{m^2}}{k} \tag{11.11}$$

$$r_0 = \frac{m\frac{L^2}{m^2}}{k(1+e)} \tag{11.12}$$

where e is the eccentricity of the ellipse and A is a constant. The equation of motion due to a central force can also be expressed in terms of the energies of the orbit. The square of the speed in polar coordinates is

$$v^2 = (\dot{r}^2 + r^2\dot{\theta}^2) \tag{11.13}$$

Since a central force is conservative, the total energy, E, is equal to the sum of the kinetic, T, and the potential, V, and is constant. The total energy is

$$\frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2) + V(r) = E = \text{ constant} \tag{11.14}$$

Substitution of the variable $u = \frac{1}{r}$ and Eq. (11.7) into Eq. (11.14) gives the orbital energy equation.

$$\frac{1}{2}m\frac{L^2}{m^2}\left(\frac{\partial^2 u}{\partial\theta^2} + u^2\right) + V(u^{-1}) = E \tag{11.15}$$

Because the potential energy function $V(r)$ for an inverse-squared force field is

$$V(r) = -\frac{k}{r} = -ku \tag{11.16}$$

the energy equation of the orbit, Eq. (11.15),

$$\frac{1}{2}m\frac{L^2}{m^2}\left(\frac{\partial^2 u}{\partial\theta^2} + u^2\right) - ku = E \tag{11.17}$$

which has the solution

$$r = \frac{m\frac{L^2}{m^2}k^{-1}}{1 + \left(1 + 2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta} \tag{11.18}$$

where the eccentricity, e, is

$$e = \left(1 + 2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2} \tag{11.19}$$

Eq. (11.19) permits the classification of the orbits according to the total energy, E, as follows:

$E < 0,$	$e < 1$	closed orbits (ellipse or circle)
$E = 0,$	$e = 1$	parabolic orbit
$E > 0,$	$e > 1$	hyperbolic orbit

Since $E = T + V$ and is constant, the closed orbits are those for which $T < |V|$, and the open orbits are those for which $T \geq |V|$. It can be shown that the time average of the kinetic energy, $< T >$, for elliptical motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, $|< V >|$. $< T >= 1/2 |< V >|$ [1].

As demonstrated in the One-Electron Atom section, the electric inverse-squared force is conservative; thus, the angular momentum of the electron, $\hbar$, and the energy of atomic orbitspheres are constant. In addition, the orbitspheres are nonradiative when the boundary condition is met.

The central force equation, Eq. (11.14), has orbital solutions, which are circular, elliptical, parabolic, or hyperbolic. The former two types of solutions are associated with atomic and molecular orbitals. These solutions are nonradiative. The boundary condition for nonradiation given in the One-Electron Atom section, is the absence of components of the spacetime Fourier transform of the current-density function synchronous with waves traveling at the speed of light. The boundary condition is met when the velocity for the charge density at every coordinate position on the orbitsphere is

$$v_n = \frac{\hbar}{m_e r_n} \tag{11.20}$$

The allowed velocities and angular frequencies are related to r_n by

$$v_n = r_n \omega_n \tag{11.21}$$

$$\omega_n = \frac{\hbar}{m_e r_n^2} \tag{11.22}$$

As demonstrated in the One-Electron Atom section and by Eq. (11.22), this condition is met for the product function of a radial Dirac delta function and a time harmonic function where the angular frequency, ω, is constant and given by Eq. (11.22).

$$\omega_n = \frac{\hbar}{m_e r_n^2} = \frac{\frac{\pi L}{m_e}}{A} \tag{11.23}$$

where L is the angular momentum and A is the area of the closed orbit. Consider the solution of the central force equation comprising the product of a two-dimensional ellipsoid and a time harmonic function. The spatial part of the product function is the convolution of a radial Dirac delta function with the equation of an ellipsoid. The Fourier transform of the convolution of two functions is the product of the individual Fourier transforms of the functions; thus, the boundary condition is met for an ellipsoidal-time harmonic function when

$$\omega_n = \frac{\pi\hbar}{m_e A} = \frac{\hbar}{m_e ab} \tag{11.24}$$

where the area of an ellipse is

$$A = \pi ab \tag{11.25}$$

where b and $2b$ are the lengths of the semiminor and minor axes, respectively, and a and $2a$ are the lengths of the semimajor and major axes, respectively. The geometry of molecular hydrogen is ellipsoidal with the internuclear axis as the principal axis; thus, the electron orbital is a two-dimensional ellipsoidal-time harmonic function. The mass follows an elliptical path, time harmonically as determined by the central field of the protons at the foci. Rotational symmetry about the internuclear axis further determines that the orbital is a prolate spheroid. In general, ellipsoidal orbits of molecular bonding, hereafter referred to as ellipsoidal molecular orbitals (MOs), have the general equation

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \tag{11.26}$$

The semiprincipal axes of the ellipsoid are a, b, c.

In ellipsoidal coordinates the Laplacian is

$$(\eta - \zeta) R_\xi \frac{\partial}{\partial \xi}\left(R_\xi \frac{\partial \phi}{\partial \xi}\right) + (\zeta - \xi) R_\eta \frac{\partial}{\partial \eta}\left(R_\eta \frac{\partial \phi}{\partial \eta}\right) + (\xi - \eta) R_\zeta \frac{\partial}{\partial \zeta}\left(R_\zeta \frac{\partial \phi}{\partial \zeta}\right) = 0 \tag{11.27}$$

An ellipsoidal MO is equivalent to a charged perfect conductor (i.e. no dissipation to current flow) whose surface is given by Eq. (11.26). It is a two-dimensional equipotential membrane where each MO is supported by the outward centrifugal force due to the corresponding angular velocity, which conserves its angular momentum of $\hbar$. It satisfies the boundary conditions for a discontinuity of charge in Maxwell's equations, Eq. (11.48). It carries a total charge $q = -e$, and it's potential is a solution of the Laplacian in ellipsoidal coordinates, Eq. (11.27).

Excited states of orbitspheres are discussed in the Excited States of the One-Electron Atom (Quantization) section. In the case of ellipsoidal MOs, excited electronic states are created when photons of discrete frequencies are trapped in the ellipsoidal resonator cavity of the MO. The photon changes the effective charge at the MO surface where the central field is ellipsoidal and arises from the protons and the effective charge of the "trapped photon" at the foci of the MO. Force balance is achieved at a series of ellipsoidal equipotential two-dimensional surfaces confocal with the ground state ellipsoid. The "trapped photons" are solutions of the Laplacian in ellipsoidal coordinates, Eq. (11.27).

As is the case with the orbitsphere, higher and lower energy states are equally valid. The photon standing wave in both cases is a solution of the Laplacian in ellipsoidal coordinates. For an ellipsoidal resonator cavity, the relationship between an allowed circumference, $4aE$, and the photon standing wavelength, λ, is

$$4aE = n\lambda \tag{11.28}$$

where n is an integer and where the elliptic integral E of Eq. (11.28) is given by

$$E(k) = \int_0^{\frac{\pi}{2}} \sqrt{1 - k\sin^2\phi}\, d\phi \tag{11.29}$$

$$k = e = \frac{\sqrt{a^2 - b^2}}{a} \tag{11.30}$$

Applying Eqs. (11.28) and (11.29-11.30), the relationship between an allowed angular frequency given by Eq. (11.24) and the photon standing wave angular frequency, ω, is:

$$\frac{\pi\hbar}{m_e A} = \frac{\hbar}{m_e n a_1 n b_1} = \frac{\hbar}{m_e a_n b_n} = \frac{1}{n^2}\omega_1 = \omega_n \tag{11.31}$$

where $n = 1, 2, 3, 4, \ldots$

$$n = \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \ldots$$

ω_1 is the allowed angular frequency for $n = 1$

a_1 and b_1 are the allowed semimajor and semiminor axes for $n = 1$

The potential, ϕ, and distribution of charge, σ, over the conducting surface of an ellipsoidal MO are sought given the conditions: 1.) the potential is equivalent to that of a charged ellipsoidal conductor whose surface is given by Eq. (11.26), 2.) it carries a total charge $q = -e$, and 3.) initially there is no external applied field. To solve this problem, a potential function must be found which satisfies Eq. (11.27), which is regular at infinity, and which is constant over the given ellipsoid. The solution is well known and is given after Stratton [2]. Consider that the Laplacian is solved in ellipsoidal coordinates wherein ξ is the parameter of a family of ellipsoids all confocal with the standard surface $\xi = 0$ whose axes have the specified values a, b, c. The variables ζ and η are the parameters of confocal hyperboloids and as such serve to measure position on any ellipsoid $\xi = \text{constant}$. On the surface $\xi = 0$; therefore, ϕ must be independent of ζ and η. Due to the uniqueness property of solutions of the Laplacian, a function which satisfies Eq. (11.27), behaves

properly at infinity, and depends only on ξ, can be adjusted to represent the potential correctly at any point outside the ellipsoid $\xi = 0$.

Thus, it is assumed that $\phi = \phi(\xi)$. Then, the Laplacian reduces to

$$\frac{\partial}{\partial \xi}(R_\xi \frac{\partial \phi}{\partial \xi}) = 0 \qquad R_\xi = \sqrt{(\xi + a^2)(\xi + b^2)(\xi + c^2)} \tag{11.32}$$

which on integration leads to

$$\phi(\xi) = C_1 \int_\xi^\infty \frac{\partial \xi}{R_\xi} \tag{11.33}$$

where C_1 is an arbitrary constant. The upper limit is selected to ensure the proper behavior at infinity. When ξ becomes very large, R_ξ approaches $\xi^{3/2}$ and

$$\phi \sim \frac{2C_1}{\sqrt{\xi}} \qquad (\xi \to \infty) \tag{11.34}$$

Furthermore, the equation of an ellipsoid can be written in the form

$$\frac{x^2}{1+\frac{a^2}{\xi}} + \frac{y^2}{1+\frac{b^2}{\xi}} + \frac{z^2}{1+\frac{c^2}{\xi}} = \xi \tag{11.35}$$

If $r^2 = x^2 + y^2 + z^2$ is the distance from the origin to any point on the ellipsoid ξ, it is apparent that as ξ becomes very large $\xi \to r^2$. Thus, at great distances from the origin, the potential becomes that of a point charge at the origin:

$$\phi \sim \frac{2C_1}{r} \tag{11.36}$$

The solution Eq. (11.33) is, therefore, regular at infinity, and the constant C_1 is then determined. It has been shown by Stratton [2] that whatever the distribution, the dominant term of the expansion at remote points is the potential of a point charge at the origin equal to the total charge of the distribution—in this case q. Hence $C_1 = \frac{q}{8\pi\varepsilon_o}$, and the potential at any point is

$$\phi(\xi) = \frac{q}{8\pi\varepsilon_o} \int_\xi^\infty \frac{\partial \xi}{R_\xi} \tag{11.37}$$

The equipotential surfaces are the ellipsoids $\xi = \text{constant}$. Eq. (11.37) is an elliptic integral and its values have been tabulated [3].

Since the distance along a curvilinear coordinate u^1 is measured not by du^1 but by $h_1 du^1$, the normal derivative in ellipsoidal coordinates is given by

$$\frac{\partial \phi}{\partial n} = \frac{1}{h_1}\frac{\partial \phi}{\partial \xi} = \frac{-q}{4\pi\varepsilon_o}\frac{1}{\sqrt{(\xi-\eta)(\xi-\zeta)}} \tag{11.38}$$

where

$$h_1 = \frac{1}{2}\frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi} \tag{11.39}$$

The density of charge, σ, over the surface $\xi = 0$ is

$$\sigma = \varepsilon_o\left(\frac{\partial \phi}{\partial n}\right)_{\xi=0} = \frac{q}{4\pi\sqrt{\eta\zeta}} \tag{11.40}$$

Defining x, y, z in terms of ξ, η, ζ, we put $\xi = 0$, it may be easily verified that

$$\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4} = \frac{\zeta\eta}{a^2b^2c^2} \qquad (\xi = 0) \tag{11.41}$$

Consequently, the charge density in rectangular coordinates is

$$\sigma = \frac{q}{4\pi abc}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{11.42}$$

(The mass-density function of an MO is equivalent to its charge-density function where m replaces q of Eq. (11.42)). The equation of the plane tangent to the ellipsoid at the point x_0, y_0, z_0 is

$$X\frac{x_0}{a^2}+Y\frac{y_0}{b^2}+Z\frac{z_0}{c^2} = 1 \tag{11.43}$$

where X, Y, Z are running coordinates in the plane. After dividing through by the square root of the sum of the squares of the coefficients of X, Y, and Z, the right member is the distance D from the origin to the tangent plane. That is,

$$D = \frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{11.44}$$

so that for an electron MO

$$\sigma = \frac{-e}{4\pi abc}D \tag{11.45}$$

In other words, the surface density at any point on a charged ellipsoidal conductor is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent

to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin.

In the case of hydrogen-type molecules and molecular ions, rotational symmetry about the internuclear axis requires that two of the axes be equal. Thus, the MO is a spheroid, and Eq. (11.37) can be integrated in terms of elementary functions. If $a > b = c$, the spheroid is prolate, and the potential is given by

$$\phi = \frac{1}{8\pi\varepsilon_o}\frac{-e}{\sqrt{a^2-b^2}}\ln\frac{\sqrt{\xi+a^2}+\sqrt{a^2-b^2}}{\sqrt{\xi+a^2}-\sqrt{a^2-b^2}} \tag{11.46}$$

SPHEROIDAL FORCE EQUATIONS

Electric Force

The spheroidal MO is a two-dimensional surface of constant potential given by Eq. (11.46) for $\xi = 0$. For an isolated electron MO the electric field inside is zero as given by Gauss' Law

$$\int_S \mathbf{E}dA = \int_V \frac{\rho}{\varepsilon_o}dV \tag{11.47}$$

where the charge density, ρ, inside the MO is zero. Gauss' Law at a two-dimensional surface with continuity of the potential across the surface according to Faraday's law in the electrostatic limit [4-6] is

$$\mathbf{n}\bullet(\mathbf{E}_1-\mathbf{E}_2)=\frac{\sigma}{\varepsilon_0} \tag{11.48}$$

$\mathbf{E}_2$ is the electric field inside which is zero. The electric field of an ellipsoidal MO with semimajor and semiminor axes a and $b = c$, respectively, is given by substituting σ given by Eq. (11.38-11.42) into Eq. (11.48).

$$\mathbf{E} = \frac{\sigma}{\varepsilon_o}\mathbf{i}_\xi = \frac{-e}{4\pi\varepsilon_o}\frac{1}{\sqrt{(\xi-\eta)(\xi-\zeta)}}\mathbf{i}_\xi = \frac{-e}{4\pi\varepsilon_o abc}D\mathbf{i}_\xi = \frac{-e}{4\pi\varepsilon_o abc}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.49}$$

wherein the ellipsoidal-coordinate parameter $\xi = 0$ at the surface of the MO and D is the distance from the origin to the tangent plane given by Eq. (11.44). The electric field and thus the force and potential energy between the protons and the electron MO can be solved based on three principles: (1) Maxwell's equations require that the electron MO is a equipotential energy surface that is a function of ξ alone; thus, it is a prolate spheroid, (2) stability to

radiation, and conservation first principles require that the angular velocity is constant and given in polar coordinates with respect to the origin by Eq. (11.24), and (3) the equations of motion due to the central force of each proton (Eqs. (11.5-11.19) and Eqs. (11.68-11.70)) also determine that the current is ellipsoidal, and based on symmetry, the current is a prolate spheroid. Thus, based on Maxwell's equations, conservation principles, and Newton's Laws for the equations of motion, the electron MO constraints and the motion under the force of the protons both give rise to a prolate spheroid. Since the energy of motion is determined from the Coulombic central field (Eqs. (11.5-11.19), the protons give rise to a prolate spheroidal energy surface (a surface of constant energy) that is matched to the equipotential, prolate spheroidal electron MO.

The force balance equation between the protons and the electron MO is solved to give the position of the foci, then the total energy is determined including the repulsive energy between the two protons at the foci to determine whether the original assumption of an elliptic orbit was valid. If the condition that $E<0$ is met, then the problem of the stable elliptic orbit is solved. In any case that this condition is not found to be met, then a stable orbit can not be formed.

The force and energy equations of a point charge(mass) (Eqs. (11.5-11.24)) are reformulated in term of densities for charge, current, mass, momentum, and potential, kinetic, and total energies. Consider an elliptical orbit shown in Figure 1 that applies to a point charge(mass) as well as a point on a continuous elliptical current loop that comprises a basis element of the continuous current density of the ellipsoidal MO. The tangent plane at any point on the ellipsoid makes equal angles with the foci radii at that point and the sum of the distance to the foci is a constant, $2a$. Thus, the normal is the bisector of the angle between the foci radii at that point as shown in Figure 1.

The unit vector normal to the ellipsoidal MO at a point (x,y,z) is

$$\hat{\mathbf{d}}=\frac{\left(\frac{x}{a^2},\frac{y}{b^2},\frac{z}{b^2}\right)}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{11.50}$$

$F_1(r(t))$ and $F_2(r(t))$ are defined as the components of the central forces centered on F_1 and F_2. The components of the central forces that are normal to the ellipsoidal MO in the direction of $\hat{\mathbf{d}}$, the unit vector in the $\mathbf{i}_\xi$-direction are defined as $F_{1\perp}(r(t))$ and $F_{2\perp}(r(t))$.

The normalized projections or projection factor of the sum of these central forces in the $\hat{\mathbf{d}}$-direction at the point (x,y,z) is

$$\begin{aligned}\frac{F_{1\perp}(r(t))+F_{2\perp}(r(t))}{\left|F_1(r(t))+F_2(r(t))\right|} &= \frac{(\mathbf{r}_1+\mathbf{r}_2)\cdot\hat{\mathbf{d}}}{2a} \\ &= \frac{\left((x-c,y,z)+(x-c,y,z)\right)\cdot\left(\frac{x}{a^2}+\frac{y}{b^2}+\frac{z}{b^2}\right)}{2a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \\ &= \frac{\left(\frac{x^2-cx}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{b^2}\right)+\left(\frac{x^2+cx}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{b^2}\right)}{2a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \\ &= \frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\end{aligned} \tag{11.51}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the radial vectors of the central forces from the corresponding focus to the point (x,y,z) on the ellipsoidal MO.

The polar-coordinate elliptical orbit of a point charge due to its motion in a central inverse-squared-radius field is given by Eqs. (11.10-11.12) as the solution of the polar-coordinate-force equations, Eqs. (11.5-11.19) and (11.68-11.70). The orbit is also completely specified in Cartesian coordinates by the solution of Eqs. (11.5-11.19) and (11.68-11.70) for the semimajor and semiminor axes. Then, the corresponding polar-coordinate elliptical orbit is given as a plane cross section through the foci of the Cartesian-coordinate-system ellipsoid having the same axes given by Eq. (11.26) where $c=b$. Thus, the Columbic central force can be determined in terms of the general Cartesian coordinates from the polar-coordinate central force equations (Eqs. (11.5-11.19)). Consider separately the elliptical solution at each focus given in polar coordinates by Eq. (11.10):

$$r_1 = a(1-e)\frac{1+e}{1+e\cos\theta} = \frac{a(1-e^2)}{1+e\cos\theta} \tag{11.52}$$

$$r_2 = \frac{a(1-e^2)}{1+e\cos(\theta+\pi)} = \frac{a(1-e^2)}{1-e\cos\theta} \tag{11.53}$$

where

$$r_0 = a-c' = a\left(1-\frac{c'}{a}\right) = a(1-e) \tag{11.54}$$

The magnitude of the sum of the central forces centered on F_1 and F_2 that are normal to the ellipsoidal MO are

$$\begin{aligned}\left|F_1(r_1)\right|+\left|F_2(r_2)\right| &= \frac{k}{r_1^2}+\frac{k}{r_2^2} \\ &= k\frac{(1+e\cos\theta)^2+(1-e\cos\theta)^2}{a^2(1-e^2)^2} \\ &= k\frac{1+2e\cos\theta+e^2\cos^2\theta+1-2e\cos\theta+e^2\cos^2\theta}{a^2(1-e^2)^2} \\ &= k\frac{1+e^2\cos^2\theta+1+e^2\cos^2\theta}{a^2(1-e^2)^2} \\ &= k\frac{2+2e^2\cos^2\theta}{a^2(1-e^2)^2}\end{aligned} \tag{11.55}$$

The vector central forces centered on F_1 and F_2 that are normal to the ellipsoidal MO are then given by the product of the corresponding magnitude and vector projection given by Eqs. (11.55) and (11.51), respectively:

$$\mathbf{F}_{1\perp}(r_1)+\mathbf{F}_{2\perp}(r_2) = k\frac{2+2e^2\cos^2\theta}{a^2(1-e^2)^2}\frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.56}$$

Eq. (11.56) is based on a single point charge e. For a charge-density distribution that is given as an ellipsoidal equipotential, the θ-dependence must vanish. In addition to the elliptical orbit being completely specified in Cartesian coordinates by the solution of Eqs. (11.5-11.19) and Eqs. (11.68-11.70) for the semimajor and semiminor axes in Eq. (11.26), the polar-coordinate elliptical orbit is also completely specified by the total constant total energy E and the angular momentum which for the electron is the constant $\hbar$. Considering Eq. (11.56), the corresponding total energy of the electron is conserved and is determined by the integration over the MO to give the average:

$$\mathbf{F}_{1\perp}(r_1)+\mathbf{F}_{2\perp}(r_2) = k\frac{2+e^2}{a^2(1-e^2)^2}\frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.57}$$

Eq. (11.57) is transformed from a two-centered-central force to a one-centered-central force to match the form of the potential of the ellipsoidal MO. In this case,

$$\mathbf{r}_1,\mathbf{r}_2 \to r(t)\mathbf{i}_\xi \tag{11.58}$$

In the case that

$$r_1 = r_2 = a \tag{11.59}$$

then,

$$r(t) = b \tag{11.60}$$

and the one-centered-central force is in the $\mathbf{i}_\xi$ -direction. Thus, Eq. (11.57) transforms as

$$\begin{aligned}\mathbf{F}_{1\perp}(r(t)) + \mathbf{F}_{2\perp}(r(t)) &= k\frac{(1-e^2)^2}{b^2(2+e^2)}\frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \\ &= \frac{2+e^2}{(1-e^2)^2}k\frac{1}{ab^2\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi\end{aligned} \tag{11.61}$$

Eq. (11.61) has the same form as that of the electric field of the ellipsoidal MO given by Eq. (11.49), except for the scaling factor of two-centered coordinates h_{2cc} :

$$h_{2cc} = \frac{2+e^2}{(1-e^2)^2} \tag{11.62}$$

As shown in the case of the derivation of the Laplacian charge-density and electric field, if $r^2 = x^2 + y^2 + z^2$ is the distance from the origin to any point on the ellipsoid ξ, it is apparent that as ξ becomes very large $\xi \to r^2$. Thus, at great distances from the origin, the potential becomes that of a point charge at the origin as given by Eq. (11.36). The same boundary condition applies to the potential and field of the protons. The limiting case is also given as $e \to 0$. Then, to transform the scale factor to that of one-centered coordinates for an ellipsoidal MO, the reciprocal of the scaling factor multiplies the Laplacian-MO-electric-field term. The reciprocal of Eq. (11.62) is

$$h_{2cc}^{-1} = \frac{(1-e^2)^2}{2+e^2} \tag{11.63}$$

such that as $e \to 0$, $h_{2cc}^{-1} \to \frac{1}{2}$. This transform scale factor corresponds to the interchange of the points of highest and lowest velocity on the surface and the distribution of the charge-density in the opposite manner as shown *infra*. The charge-density distribution corrects the angular variation in central force over the surface such that a solution of the central force equation of motion and the Laplacian MO are solved simultaneously. It can also be considered as a multipole normalization factor such those of the spherical harmonics and the

spherical geometric factor of atomic electrons that gives the central force as a function of ξ only.

The reciprocal of the h_{2cc} form-factor with the dependence of the charge density on the distance parameter $r(t)$ gives

$$\mathbf{F}_{1\perp}(r(t))+\mathbf{F}_{2\perp}(r(t))=k\frac{(1-e^2)^2}{b^2(2+e^2)}\frac{1}{a\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.64}$$

From Eq. (11.31), the magnitude of the ellipsoidal field corresponding to a below "ground state" hydrogen-type molecular ion is an integer p. The integer is one in the case of the hydrogen molecular ion and an integer greater than one in the case of each dihydrino molecular ion. The central-electric-force constant, k, from the two protons that includes the central-field contribution due photons of lower-energy states is

$$k=\frac{Ze^2}{4\pi\varepsilon_0}=\frac{p2e^2}{4\pi\varepsilon_0} \tag{11.65}$$

Substitution of Eq. (11.65) for k in Eq. (11.64) gives the one-center-coordinate electric force $\mathbf{F}_{ele}$ between the protons and the ellipsoidal MO:

$$\mathbf{F}_{ele}=\mathbf{F}_{1\perp}(r(t))+\mathbf{F}_{2\perp}(r(t))=\frac{2pe^2}{4\pi\varepsilon_0}\frac{\left(1-\left(\frac{c'}{a}\right)^2\right)^2}{ab^2\left(2+\left(\frac{c'}{a}\right)^2\right)}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}\mathbf{i}_\xi \tag{11.66}$$

where e is the charge and with the distance from the origin to a nucleus at a focus defined as c', the eccentricity, e, is

$$e=\frac{c'}{a} \tag{11.67}$$

From the orbital equations in polar coordinates, Eqs. (11.10-11.12), the following relationship can be derived [1]:

$$a=\frac{m\frac{L^2}{m^2}}{k(1-e^2)} \tag{11.68}$$

For any ellipse,

$$b=a\sqrt{1-e^2} \tag{11.69}$$

Thus,

$$b = a\sqrt{\frac{\frac{L^2}{m^2}m}{ka}}\text{ (point charge (mass) in polar coordinates)} \tag{11.70}$$

From, the equal energy condition, it can be shown that b for the motion of a point charge (mass) in polar coordinates due to a proton at one focus corresponds to

$$c' = \sqrt{a^2 - b^2} \tag{11.71}$$

of the MO in ellipsoidal coordinates, and k_1 of one attracting focus is replaced by $k = 2k_1$ of ellipsoidal coordinates with two attracting foci. In ellipsoidal coordinates, k is given by Eq. (11.65) and L for the electron equals $\hbar$.

Consider the force balance equation for the point on the ellipse at the intersection of the semiminor axis b with the ellipse. At this point called $(0,b)$, the distances from each focus, r_1 and r_2, to the ellipse are equal. The relationship for the sum of the distances from the foci to any point on the ellipse is

$$r_1 + r_2 = 2a \tag{11.72}$$

Thus, at point $(0,b)$,

$$r_1 = r_2 = a \tag{11.73}$$

Using Eq. (11.5), the magnitude of the force balance in the radial ($r(t)$) direction, from the origin, is given by

$$mr\dot{\theta}^2 = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\sin\theta = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\frac{b}{a} \tag{11.74}$$

wherein the $m\ddot{r}$ term is zero and θ is the angle from the focus to point $(0,b)$. Using Eqs. (11.24), (11.94), and (11.95), Eq. (11.74) becomes

$$mr\omega^2 = mb\frac{\hbar^2}{m^2a^2b^2} = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\frac{b}{a} \tag{11.75}$$

In order for the prolate spheroidal MO to be an equipotential surface, the mass and charge density must be according to Eq. (11.45). In this case, the mass and charge density along the ellipse is such that the magnitudes of the radial and transverse forces components at point $(0,b)$ are equivalent. Furthermore, according to Eq. (11.5), the central force of each proton at a focus is separable and symmetrical to that at the other focus. Based on symmetry, the transverse forces of the two protons are in opposite directions and the radial components are in the same direction. But, the relationship between the magnitudes must still hold wherein at

point $(0,b)$ the transverse force is equivalent to that due to the sum of the charges at one focus. The sum of the magnitudes of the transverse forces which is equivalent to a force of $2e$ at each focus in turn is

$$\left|f(r)e_\theta\right| = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\cos\theta = \frac{2pe^2}{4\pi\varepsilon_0 a^2}\frac{c'}{a} \tag{11.76}$$

Thus, using the mass and charge-density scaling factor, $\frac{\frac{c'}{a}}{\frac{b}{a}} = \frac{c'}{b}$, to match the equipotential condition in Eq. (75) gives

$$b\frac{\hbar^2}{m_e\frac{c'}{b}a^2b^2} = \frac{2\frac{c'}{b}pe^2}{4\pi\varepsilon_0 a^2}\frac{b}{a} \tag{11.77}$$

$$c'^2 = \frac{\hbar^2 4\pi\varepsilon_0 a}{m_e 2pe^2} \tag{11.78}$$

Using Eq. (1.235)

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{me^2 2pa}} = \sqrt{\frac{aa_0}{2p}} \tag{11.79}$$

Then, the length of the semiminor axis of the prolate spheroidal MO, $b = c$, is

$$b = \sqrt{a^2 - c'^2} \tag{11.80}$$

Correspondingly, c' is given by Eq. (11.71).

Substitution of Eq. (11.79) into Eq. (11.66) gives the electric force:

$$\mathbf{F}_{ele} = \frac{2pe^2}{4\pi\varepsilon_0} \frac{\left(1-\left(\frac{\sqrt{\frac{aa_0}{2p}}}{a}\right)^2\right)^2}{ab^2\left(2+\left(\frac{\sqrt{\frac{aa_0}{2p}}}{a}\right)^2\right)} \frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \mathbf{i}_\xi$$

$$= \frac{2pe^2}{4\pi\varepsilon_0} \frac{\left(1-\frac{a_0}{2ap}\right)^2}{ab^2\left(2+\frac{a_0}{2ap}\right)} \frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \mathbf{i}_\xi \qquad (11.81)$$

$$= \frac{2pe^2}{4\pi\varepsilon_0} \frac{\left(1-\frac{a_0}{2ap}\right)^2}{ab^2\left(2+\frac{a_0}{2ap}\right)} D\mathbf{i}_\xi$$

Centrifugal Force

The centrifugal force along the radial vector from each proton at each focus of the ellipsoid is given by the $mr\dot{\theta}^2$ term of Eq. (11.5). The tangent plane at any point on the ellipsoid makes equal angles with the foci radii at that point and the sum of the distance to the foci is a constant, $2a$. Thus, the normal is the bisector of the angle between the foci radii at that point as shown in Figure 1. In order to satisfy the equation of motion for an equal energy surface for both foci, the transverse component of the central force of one foci at any point on the elliptic orbit due to the central force of the other (Eq. (11.5)) must cancel on average and vice versa. Thus, the centrifugal force due to the superposition of the central forces in the direction of each foci must be normal to an ellipsoidal surface in the direction perpendicular to the direction of motion. Thus, it is in the ξ-direction. This can be only be achieved by a time rate of change of the momentum density that compensates for the variation of the distances from each focus to each point on an elliptical cross section. Since the angular momentum must be conserved, there can be no net force in the direction transverse to the elliptical path over each orbital path. The total energy must also be conserved; thus, as shown *infra.* the distribution of the mass must also be a solution of Laplace's equation in the parameter ξ only. Thus, the mass-density constraint is the same as the charge-density constraint. As further shown *infra.*, the distribution and concomitantly the centrifugal force is

a function of D, the time-dependent distance from the center of the ellipsoid to a tangent plane given by Eq. (11.44) where D and the Cartesian coordinates are the time-dependent parameters.

Each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptical plane cross section of the spheroidal MO through the foci. The kinetic energy of the electron is conserved. Then, the corresponding radial conservative force balance equation is

$$m(\ddot{r} + C_1 r) = 0 \tag{11.82}$$

The motion is such that eccentric angle, θ, changes at a constant rate at each point. That is $\theta = \omega t$ at time t where the angular velocity ω is a constant. The solution of the homogeneous equation with $C_1 = \omega^2$ is

$$r(t) = \mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t \tag{11.83}$$

where a is the semimajor axis, b is semiminor axis, and the boundary conditions of $r(t) = a$ for $\omega t = 0$ and $r(t) = b$ for $\omega t = \frac{\pi}{2}$ were applied. Eq. (11.83) is the parametric equation of the ellipse of the orbit. The velocity is given by the time derivative of the parametric position vector:

$$v(t) = \dot{r}(t) = -\mathbf{i}a\omega\sin\omega t + \mathbf{j}b\omega\cos\omega t \tag{11.84}$$

The velocity is $\frac{\pi}{2}$ out of phase with the charge density at $r(t) = a$ ($\omega t = 0$) and $r(t) = b$ ($\omega t = \frac{\pi}{2}$) such that the lowest charge density has the highest velocity and the highest charge density has the lowest velocity. In this case, it can be shown that the current is constant along each elliptical path of the MO. Recall that nonradiation results when ω = constant given by Eq. (11.24) that corresponds to a constant current, which further maintains the current continuity condition.

Consider Eq. (11.32) for the prolate spheroidal MO. From this equation, the mass and current-densities, the angular momentum, and the potential and kinetic energies are a function of ξ alone, and any dependence on the orthogonal coordinate parameters averages to unity. From Eq. (11.32),

$$R_\xi \frac{\partial \phi}{\partial \xi} = C_1 \tag{11.85}$$

Substitution of Eq. (11.40) into Eq. (11.85) gives

$$\int_{\xi}^{\infty} R_{\xi} h_1 \frac{e}{4\pi\sqrt{\eta\zeta}} \delta(\xi)\, d\xi = \varepsilon_0 C_1 = \frac{e}{8\pi} \tag{11.86}$$

where C_1 is from Eq. (11.36). Substitution of Eq. (11.39) into Eq. (11.86) gives

$$\int_{\xi}^{\infty} R_{\xi} \frac{e}{4\pi\sqrt{\eta\zeta}} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi)\, d\xi = \frac{e}{8\pi} \tag{11.87}$$

Comparison of Eq. (11.86) with Eq. (11.87) demonstrates that the

$$8\pi \int_{\xi}^{\infty} R_{\xi} \frac{e}{4\pi\sqrt{\eta\zeta}} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi)\, d\xi = e \tag{11.88}$$

The current density J is given by the product of the constant frequency (Eq. (11.24)) and the charge density (Eq. (11.40)):

$$J = \frac{\hbar}{2\pi m_e ab} \frac{e}{4\pi\sqrt{\eta\zeta}} \tag{11.89}$$

The total constant current is dependent on ξ alone according to Eq. (11.32). Then, applying the result of Eq. (11.88) to Eq. (11.89) gives

$$\mathbf{i} = 8\pi \int_{\xi}^{\infty} R_{\xi} \frac{\hbar}{2\pi m_e ab} \frac{e}{4\pi\sqrt{\eta\zeta}} \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_{\xi}} \delta(\xi)\, d\xi\ \mathbf{e}_{\zeta} \times \mathbf{e}_{\xi} = \frac{e\hbar}{2\pi m_e ab}\ \mathbf{e}_{\eta} \tag{11.90}$$

the constant current that is nonradiative.

If $\mathbf{a}(t)$ denotes the acceleration vector, then

$$\mathbf{a}(t) = -\omega^2 r(t) \mathbf{i}_r \tag{11.91}$$

In other words, the acceleration is centrifugal as in the case of circular motion with constant angular speed ω. The dot product of $\mathbf{r}(t)$ with $\hat{\mathbf{d}}$, the unit vector normal to the ellipsoidal MO at a point (x, y, z) given by Eq. (11.50), is

$$\mathbf{r}(t) \cdot \hat{\mathbf{d}} = \frac{(x, y, z) \cdot \left(\frac{x}{a^2}, \frac{y}{b^2}, \frac{z}{b^2} \right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} = \frac{\left(\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{b^2} \right)}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} \tag{11.92}$$

Using Eq. (11.26), the normal component projection is

$$\mathbf{r}(t) \cdot \hat{\mathbf{d}} = \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}} = D \tag{11.93}$$

where D, the distance from the origin to the tangent plane, is given by Eq. (11.44).

The centrifugal force, $\mathbf{F}_{ci}$, on mass element m_i [7] given by the second term of Eq. (11.82) is

$$\mathbf{F}_{ci} = m_i a = -m_i \omega^2 r(t) \tag{11.94}$$

Substitution of the angular velocity given by Eq. (11.24) and m_e for m into Eq. (11.94) gives the centrifugal force $\mathbf{F}_c$ on the electron that is normal to the MO surface according to Eq. (11.93):

$$\mathbf{F}_c = \frac{-\hbar^2}{m_e a^2 b^2} \mathbf{r}(t) \cdot \hat{\mathbf{d}} \mathbf{i}_\xi = \frac{-\hbar^2}{m_e a^2 b^2} D \mathbf{i}_\xi \tag{11.95}$$

$\mathbf{F}_c$ has an equivalent dependence on D as the electric force based on the charge distribution (Eq. (11.45)). This is expected based on the invariance of $\frac{e}{m_e}$ which results in the same distribution of the mass and charge.

The equipotential charge-density distribution gives rise to the constant current condition. It also gives rise to a constant total kinetic energy condition wherein the angular velocity given by Eq. (11.24) is a constant. Recall from Eq. (11.32), that on the surface $\xi = 0$; ϕ must be independent of ζ and η and depend only on ξ at any point outside the ellipsoid $\xi = 0$. Since the current and total kinetic energy are also constant on the surface $\xi = 0$, the total kinetic energy depends only on ξ. Thus, the centrifugal force on the mass of the electron, m_e, must be in the same direction as the electric field corresponding to ϕ, normal to the electron surface wherein any tangential component in Eq. (11.94) averages to zero over the electron MO by the mass distribution given by Eqs. (11.40) and (11.45) with m_e replacing e.

The cancellation of tangential acceleration over each elliptical path maintains the charge density distribution given by Eq. (11.40) with constant current at each point on each elliptical path of the MO. Since the centrifugal force is given by Eq. (11.94), the multiplication of the mass density by the scaling factor h_1 and integration with respect to ξ gives a constant net centrifugal force. Thus, the result matches those of the determination of the constant current (Eq. (11.90)) and angular momentum shown *infra.* (Eq. (11.101)) wherein the charge and mass densities given in Eqs. (11.90-11.91) and (11.100), respectively, were integrated over.

Specifically, consider the normal-directed centrifugal force, $\mathbf{F}_{ci}$, on mass element m_i:

$$\mathbf{F}_{ci} = -m_i \omega^2 D\mathbf{i}_\xi \tag{11.96}$$

The mass density is given by Eq. (11.40) with m_e replacing e. Then, the substitution of the mass density for m_i in Eq. (11.96) and using Eq. (11.24) for ω gives the centrifugal force density $\mathbf{F}_{ca}$:

$$\mathbf{F}_{ca} = \frac{m_e}{4\pi\sqrt{\eta\zeta}} \frac{\hbar^2}{m_e^2 a^2 b^2} D\mathbf{i}_\xi \tag{11.97}$$

Eq. (11.32) determines that the centrifugal force is a function of ξ alone, and any dependence on the transverse coordinate parameters averages to zero. Using the result of Eq. (11.88) gives the net centrifugal force $\mathbf{F}_c$:

$$\mathbf{F}_c = 8\pi \int_\xi^\infty \frac{1}{4\pi\sqrt{\eta\zeta}} \frac{\hbar^2}{m_e a^2 b^2} R_\xi \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi} D\delta(\xi) d\xi \mathbf{i}_\xi = \frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi \tag{11.98}$$

In the limit as the ellipsoidal coordinates go over into spherical coordinates, Eq. (11.95) reduces to the centrifugal force of the spherical orbitsphere given by Eq. (1.232) with Eq. (1.47). This condition must be and is met as a further boundary condition that parallels that of Eqs. (11.32-11.37). Using the same dependence of the total mass(charge) on the scale factor h_1 according to Eqs. (11.32-11.40), the further boundary conditions on the angular momentum and kinetic energy are met.

Specifically, the constant potential and current conditions and the use of Eq. (11.32) in the derivation of Eq. (11.95) also satisfy another condition, the conservation of $\hbar$ of angular momentum of the electron. The angular momentum $\mathbf{p}_i$ at each point i of mass m_i is

$$\begin{aligned}
\mathbf{p}_i(t) &= m_i \mathbf{r}(t) \times \mathbf{v}(t) \\
&= m_i (\mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t) \times (-\mathbf{i}a\omega\sin\omega t + \mathbf{j}b\omega\cos\omega t) \\
&= m_i ab\omega(\cos^2\omega t + \sin^2\omega t)\mathbf{i}\times\mathbf{j} \\
&= m_i ab\omega\mathbf{k}
\end{aligned} \tag{11.99}$$

The mass density is given by Eq. (11.40) with m_e replacing e. Then, substitution of m_i in Eq. (11.99) by the mass density and using Eq. (11.24) for ω gives the angular momentum density $\mathbf{p}(t)$:

$$\mathbf{p}(t) = ab\omega \frac{m_e}{4\pi\sqrt{\eta\zeta}}\mathbf{k} = ab\frac{\hbar}{m_e ab}\frac{m_e}{4\pi\sqrt{\eta\zeta}}\mathbf{k} \tag{11.100}$$

Using the result of Eq. (11.88) gives the total constant angular momentum $\mathbf{L}$:

$$\mathbf{L} = 8\pi \int_{\xi}^{\infty} \hbar \frac{1}{4\pi\sqrt{\eta\zeta}} R_\xi \frac{1}{2} \frac{\sqrt{(\xi-\eta)(\xi-\zeta)}}{R_\xi} \delta(\xi) d\xi \mathbf{k} = \hbar \mathbf{k} \tag{11.101}$$

Eq. (11.101) demonstrates conservation of angular momentum that is a function of ξ alone that parallels the case of atomic electrons where $\mathbf{L}$ conservation is a function of the radius r alone as given by Eq. (1.57).

Similarly, the kinetic energy $T(t)$ at each point i of mass m_i is

$$\begin{aligned} T(t) &= \frac{1}{2} m_i v(t)^2 \\ &= \frac{1}{2} m_i \left(-\mathbf{i}a\omega \sin\omega t + \mathbf{j}b\omega \cos\omega t\right)^2 \\ &= \frac{1}{2} m_i \omega^2 \left(a^2 \sin^2 \omega t + b^2 \cos^2 \omega t\right) \end{aligned} \tag{11.102}$$

In Eqs. (11.96-11.98), m_i was replaced by the mass density and the ξ integral was determined to give the centrifugal force in terms of the mass of the electron. The kinetic energy can also be determined from the ξ integral of the centrifugal force:

$$T = h_{2cc} F_c \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_\xi} \tag{11.103}$$

The result is given in Eq. (11.119). From Eq. (11.102), the kinetic energy is time (position) dependent, but the total kinetic energy corresponding to the centrifugal force given by Eq. (11.95) satisfies the condition that the time-averaged kinetic energy is 1/2 the time-averaged potential energy for elliptic motion in an inverse-squared central force [1]. (Here, the potential and total kinetic energies are constant and correspond to the time-averaged energies of the general case.) Thus, as shown by Eqs. (11.122) (11.124), (11.262), and (11.264) energy is conserved.

Force Balance of Hydrogen-type Molecular Ions

Consider the case of spheroidal coordinates based on the rotational symmetry about the semimajor axis [2]. In the limit, as the focal distance $2c$ and the eccentricity of the series of confocal ellipses approaches zero, spheroidal coordinates go over into spherical coordinates with $\xi \to r$ and $\eta \to \cos\theta$. The field of an equipotential two-dimensional charge surface of constant radius $r = R$ is equivalent to that of a point charge of the total charge of the spherical shell at the origin. The force balance between the centrifugal force and the central Coulomb force for spherical symmetry is given by Eq. (1.232).

Similarly, the centrifugal force is the direction of ξ and balances the central Coulombic force between the protons at the foci and the electron MO. In the case of the prolate spheroidal MO, the inhomogeneous equation given by Eq. (11.5) must hold for each fixed position of $r(t)$ since the MO is static in time due to the constant current condition. With $r(t)$ fixed, the $m\ddot{r}$ term of Eq. (11.5) is zero, and the force balanced equation is the balance between the centrifugal force and the Coulombic force which are both normal to the surface of the elliptic orbit:

$$mr\dot{\theta}^2 = f(r) \tag{11.104}$$

Substitution of Eq. (11.81) and Eq. (11.95) into Eq. (11.104) gives the force balance between the centrifugal and electric central forces:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2pe^2}{4\pi\varepsilon_0} \frac{\left(1-\frac{a_0}{2ap}\right)^2}{ab^2\left(2+\frac{a_0}{2ap}\right)} D \tag{11.105}$$

$$\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2ap}\left(2+\frac{a_0}{2ap}\right) = \left(1-\frac{a_0}{2ap}\right)^2 \tag{11.106}$$

$$\frac{a_0}{ap}+\left(\frac{a_0}{2ap}\right)^2 = \left(1-\frac{a_0}{2ap}\right)^2 \tag{11.107}$$

$$\frac{a_0}{ap}+\left(\frac{a_0}{2ap}\right)^2 = 1-\frac{a_0}{ap}+\left(\frac{a_0}{2ap}\right)^2 \tag{11.108}$$

$$a = 2\frac{a_0}{p} \tag{11.109}$$

Substitution of a given by Eq. (11.109) into Eq. (11.79) gives

$$c' = \frac{a_0}{p} \tag{11.110}$$

The internuclear distance from Eq. (11.110) is

$$2c' = \frac{2a_o}{p} \tag{11.111}$$

Substitution of $a = \frac{2a_o}{p}$ and $c' = \frac{a_o}{p}$ into Eq. (11.80) gives the length of the semiminor axis of the prolate spheroidal MO, $b = c$:

$$b=\frac{\sqrt{3}}{p}a_o \tag{11.112}$$

Substitution of $a=\frac{2a_o}{p}$ and $c'=\frac{a_o}{p}$ into Eq. (11.67) gives the eccentricity, e:

$$e=\frac{1}{2} \tag{11.113}$$

From Eqs. (11.63-11.65), the result of Eq. (11.113) can be used to the obtain the electric force $\mathbf{F}_{ele}$ between the protons and the ellipsoidal MO as

$$\mathbf{F}_{ele}=Ze\mathbf{E}\mathbf{i}_\xi=h_{2cc}^{-1}\frac{p2e^2}{4\pi\varepsilon_o ab^2}D\mathbf{i}_\xi=\frac{pe^2}{8\pi\varepsilon_0}D\mathbf{i}_\xi \tag{11.114}$$

where the electric field $\mathbf{E}$ of the MO is given by Eq. (11.49). Then, the force balance of the hydrogen-type molecular ion is given by

$$\frac{\hbar^2}{m_e a^2 b^2}D=\frac{pe^2}{8\pi\varepsilon_0}D \tag{11.115}$$

which has the parametric solution given by Eq. (11.83) when

$$a=\frac{2a_0}{p} \tag{11.116}$$

The solutions for the prolate spheroidal axes and eccentricity are given by Eqs. (11.109-11.113).

ENERGIES OF HYDROGEN-TYPE MOLECULAR IONS

From Eq. (11.31), the magnitude of the ellipsoidal field corresponding to a below "ground state" hydrogen-type molecule is an integer, p. The force balance equation (Eq. (11.115)) applies for each point of the electron MO having non-constant charge (mass)-density and velocity over the equipotential and equal energy surface. The electron potential and kinetic energies are thus determined from an ellipsoidal integral.

The potential energy is doubled due to the transverse electric force. The force normal to the MO is given by the dot product of the sum of the force vectors from each focus with $\hat{\mathbf{d}}$ where the angle β is $\beta=\frac{\pi}{2}-\alpha$, and the transverse forces are given by the cross product with $\hat{\mathbf{d}}$. As shown in Figure 1, equivalently, the transverse projection is given with the angle α replacing β where the range of α is the same as β. The two contributions to the

potential energy doubles it. The potential energy, V_e, of the electron MO in the field of magnitude p times that of the two protons at the foci is

$$\begin{aligned} V_e &= 2\frac{-2pe^2}{4\pi\varepsilon_o} D\frac{ab^2}{2D}\int_\xi^\infty \frac{d\xi}{R_\xi} \\ &= \frac{-4pe^2}{8\pi\varepsilon_o}\int_\xi^\infty \frac{d\xi}{(\xi+b)\sqrt{\xi+a}} \\ &= \frac{-4pe^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \\ &= \frac{-4pe^2}{8\pi\varepsilon_o c'}\ln\frac{a+c'}{a-c'} \end{aligned} \tag{11.117}$$

where

$$\sqrt{a^2-b^2} = c' \tag{11.118}$$

$2c'$ is the distance between the foci which is the internuclear distance. The kinetic energy, T, of the electron MO follows from the same type of integral as V_e using Eqs. (7-14) of Stratton [8], Eqs. (11.37-11.46), and integral #147 of Lide [9]. T is given by the corresponding integral of the centrifugal force (LHS of Eq. (11.115)) with the constraint that the current motion allows the equipotential and equal energy condition with a central field due to the protons; thus, it is corrected by the scale factor h_{2cc} given by Eq. (11.62). The h_{2cc} correction can be considered the scaling factor of the moment of inertial such that the kinetic energy is equivalent to the rotational energy for constant angular frequency ω. The kinetic energy, T, of the electron MO is given by

$$T = h_{2cc}\frac{-\hbar^2}{m_e a^2 b^2} D\frac{ab^2}{2D}\int_\xi^\infty \frac{d\xi}{R_\xi} = \frac{-4\hbar^2}{2m_e a}\int_\xi^\infty \frac{d\xi}{(\xi+b)\sqrt{\xi+a}} = \frac{-2\hbar^2}{m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.119}$$

The potential energy, V_P, due to proton-proton repulsion in the field of magnitude p times that of the protons at the foci ($\xi = 0$) is

$$V_p = \frac{pe^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} \tag{11.120}$$

The total energy, E_T, is given by the sum of the energy terms

$$E_T = V_e + V_p + T \tag{11.121}$$

Substitution of a and b given by Eqs. (11.109) and (11.112), respectively, into Eqs. (11.117), (11.119), (11.120), and (11.121) gives

$$V_e = \frac{-4p^2e^2}{8\pi\varepsilon_0 a_0}\ln 3 \tag{11.122}$$

$$V_p = \frac{p^2e^2}{8\pi\varepsilon_0 a_0} \tag{11.123}$$

$$T = \frac{2p^2e^2}{8\pi\varepsilon_0 a_0}\ln 3 \tag{11.124}$$

$$E_T = -13.6\ eV(4p^2\ln 3 - p^2 - 2p^2\ln 3) = -p^2 16.28\ eV \tag{11.125}$$

The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical-mechanics equations of an ellipse that considered only the binding force between the protons and the electron and the electron centrifugal force. T is one-half the magnitude of V_e as required for an inverse-squared force [1] wherein V_e is the source of T.

VIBRATION OF HYDROGEN-TYPE MOLECULAR IONS

A charge, q, oscillating according to $\mathbf{r}_0(t) = \mathbf{d}\sin\omega_0 t$ has a Fourier spectrum

$$\mathbf{J}(\mathbf{k},\omega) = \frac{q\omega_0 d}{2} J_m(k\cos\theta d)\{\delta[\omega-(m+1)\omega_0] + \delta[\omega-(m-1)\omega_0]\} \tag{11.126}$$

where J_m's are Bessel functions of order m. These Fourier components can, and do, acquire phase velocities that are equal to the velocity of light [10]. The protons of hydrogen-type molecular ions and molecules oscillate as simple harmonic oscillators; thus, vibrating protons will radiate. Moreover, non-oscillating protons may be excited by one or more photons that are resonant with the oscillatory resonance frequency of the molecule or molecular ion, and oscillating protons may be further excited to higher energy vibrational states by resonant photons. The energy of a photon is quantized according to Planck's equation

$$E = \hbar\omega \tag{11.127}$$

The energy of a vibrational transition corresponds to the energy difference between the initial and final vibrational states. Each state has an electromechanical resonance frequency, and the emitted or absorbed photon is resonant with the difference in frequencies. Thus, as a general principle, quantization of the vibrational spectrum is due to the quantized energies of photons and the electromechanical resonance of the vibrationally excited ion or molecule.

It is shown by Fowles [11] that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit. In a circular orbit in spherical coordinates, the transverse equation of motion gives

$$\dot{\theta} = \frac{L/m}{r^2} \tag{11.128}$$

where L is the angular momentum. The radial equation of motion is

$$m\left(\ddot{r} - r\dot{\theta}^2\right) = f(r) \tag{11.129}$$

Substitution of Eq. (11.128) into Eq. (11.129) gives

$$m\ddot{r} - \frac{m(L/m)^2}{r^3} = f(r) \tag{11.130}$$

For a circular orbit, r is a constant and $\ddot{r} = 0$. Thus, the radial equation of motion is given by

$$-\frac{m(L/m)^2}{a^3} = f(a) \tag{11.131}$$

where a is the radius of the circular orbit for central force $f(a)$ at $r = a$. A perturbation of the radial motion may be expressed in terms of a variable x defined by

$$x = r - a \tag{11.132}$$

The differential equation can then be written as

$$m\ddot{x} - m(L/m)^2 (x+a)^{-3} = f(x+a) \tag{11.133}$$

Expanding the two terms involving $x+a$ as a power series in x, gives

$$m\ddot{x} - m(L/m)^2 a^{-3}\left(1 - 3\frac{x}{a} + \ldots\right) = f(a) + f'(a)x + \ldots \tag{11.134}$$

Substitution of Eq. (11.131) into Eq. (11.134) and neglecting terms involving x^2 and higher powers of x gives

$$m\ddot{x} + \left[\frac{-3}{a}f(a) - f'(a)\right]x = 0 \tag{11.135}$$

For an inverse-squared central field, the coefficient of x in Eq. (11.135) is positive, and the equation is the same as that of the simple harmonic oscillator. In this case, the particle, if perturbed, oscillates harmonically about the circle $r = a$, and an approximation of the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m}} = \sqrt{\frac{k}{m}} \tag{11.136}$$

An apsis is a point in an orbit at which the radius vector assumes an extreme value (maximum or minimum). The angle swept out by the radius vector between two consecutive apsides is called the apsidal angle. Thus, the apsidal angle is π for elliptical orbits under the inverse-squared law of force. In the case of a nearly circular orbit, Eq. (11.135) shows that r oscillates about the circle $r = a$, and the period of oscillation is given by

$$\tau_r = 2\pi \sqrt{\frac{m}{-\left[\frac{3}{a} f(a) + f'(a)\right]}} \tag{11.137}$$

The apsidal angle in this case is just the amount by which the polar angle θ increases during the time that r oscillates from a minimum value to the succeeding maximum value which is τ_r. From Eq. (11.128), $\dot{\theta} = \frac{L/m}{r^2}$; therefore, θ remains constant, and Eq. (11.131) gives

$$\dot{\theta} \approx \frac{L/m}{a^2} = \left[-\frac{f(a)}{ma}\right]^{1/2} \tag{11.138}$$

Thus, the apsidal angle is given by

$$\psi = \frac{1}{2}\tau_r \dot{\theta} = \pi\left[3 + a\frac{f'(a)}{f(a)}\right]^{-1/2} \tag{11.139}$$

Thus, the power force of $f(r) = -cr^n$ gives

$$\psi = \pi(3+n)^{-1/2} \tag{11.140}$$

The apsidal angle is independent of the size of the orbit in this case. The orbit is re-entrant, or repetitive, in the case of the inverse-squared law ($n = -2$) for which $\psi = \pi$.

A prolate spheroid MO and the definition of axes are shown in Figures 5A and 5B, respectively. Consider the two nuclei A and B, each at focus of the prolate spheroid MO. From Eqs. (11.115), (11.117), and (11.119), the attractive force between the electron and each nucleus at a focus is

$$f(a) = -\frac{pe^2}{4\pi\varepsilon_o a^2} \tag{11.141}$$

and

$$f'(a) = \frac{2pe^2}{4\pi\varepsilon_o a^3} \tag{11.142}$$

In addition to the attractive force between the electron and the nuclei, there is a repulsive force between the two nuclei that is the source of a corresponding reactive force on

the reentrant electron orbit. Consider an elliptical orbital plane cross section of the MO in the xy-plane with a nucleus A at (-c', 0) and a nucleus B at (c', 0). For B acting as the attractive focus, the reactive repulsive force at the point (a, 0), the positive semimajor axis, depends on the distance from (a, 0) to nucleus A at (-c', 0) (i.e. the distance from the position of the electron MO at the semimajor axis to the opposite nuclear repelling center at the opposite focus). The distance is given by the sum of the semimajor axis, a, and c', 1/2 the internuclear distance. The contribution from the repulsive force between the two protons is

$$f(a+c') = \frac{pe^2}{8\pi\varepsilon_o (a+c')^2} \tag{11.143}$$

and

$$f'(a+c') = -\frac{pe^2}{4\pi\varepsilon_o (a+c')^3} \tag{11.144}$$

Thus, from Eqs. (11.136) and (11.141-11.144), the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{pe^2}{4\pi\varepsilon_o a^3} - \frac{pe^2}{8\pi\varepsilon_o (a+c')^3}}{\mu}}$$

$$= \sqrt{\frac{\frac{pe^2}{4\pi\varepsilon_o \left(\frac{2a_H}{p}\right)^3} - \frac{pe^2}{8\pi\varepsilon_o \left(\frac{3a_H}{p}\right)^3}}{\mu}} \tag{11.145}$$

$$= p^2 4.44865\ X\ 10^{14}\ rad/s$$

where the semimajor axis, a, is $a = \frac{2a_H}{p}$ according to Eq. (11.116) and c' is $c' = \frac{a_H}{p}$ according to Eq. (11.110).

In the case of a hydrogen molecule or molecular ion, the electrons which have a mass of 1/1836 that of the protons move essentially instantaneously, and the charge density is that of a continuous membrane. Thus, a stable electron orbit is maintained with oscillatory motion of the protons. Hydrogen molecules and molecular ions are symmetrical along the semimajor axis; thus, the oscillatory motion of protons is along this axis. Let x be the increase in the semimajor due to the reentrant orbit with a corresponding displacement of the protons along the semimajor axis from the position of the initial foci of the stationary state. The equation of proton motion due to the perturbation of an orbit having a central inverse-squared central force [1] and neglecting terms involving x^2 and higher is given by

$$\mu\ddot{x} + kx = 0 \tag{11.146}$$

which has the solution in terms of the maximum amplitude of oscillation, A, the reduced nuclear mass, μ, the restoring constant or spring constant, k, the resonance angular frequency, ω_0, and the vibrational energy, E_{vib}, [12]

$$A\cos\omega_0 t \tag{11.147}$$

where

$$\omega_0 = \sqrt{\frac{k}{\mu}} \tag{11.148}$$

For a symmetrical displacement x, the potential energy corresponding to the oscillation E_{Pvib} is given by

$$E_{Pvib} = 2\left(\frac{1}{2}kx^2\right) = kx^2 \tag{11.149}$$

The total energy of the oscillating molecular ion, $E_{Totalvib}$, is given as the sum of the kinetic and potential energies

$$E_{Totalvib} = \frac{1}{2}\mu\dot{x}^2 + kx^2 \tag{11.150}$$

The velocity is zero when x is the maximum amplitude, A. The total energy of the oscillating molecular ion, $E_{Totalvib}$, is then given as the potential energy with $x = A$

$$E_{Totalvib} = kA^2 \tag{11.151}$$

Thus,

$$A = \sqrt{\frac{E_{Totalvib}}{k}} \tag{11.152}$$

It is shown in the Excited States of the One-Electron Atom (Quantization) section that the change in angular frequency of the electron orbitsphere (Eq. (2.21)) is identical to the angular frequency of the photon necessary for the excitation, ω_{photon} (Eq. (2.19)). The energy of the photon necessary to excite the equivalent transition in an electron orbitsphere is one-half of the excitation energy of the stationary cavity because the change in kinetic energy of the electron orbitsphere supplies one-half of the necessary energy. The change in the angular frequency of the orbitsphere during a transition and the angular frequency of the photon corresponding to the superposition of the free space photon and the photon corresponding to the kinetic energy change of the orbitsphere during a transition are equivalent. The correspondence principle holds. It can be demonstrated that the resonance condition between

these frequencies is to be satisfied in order to have a net change of the energy field [13]. The bound electrons are excited with the oscillating protons. Thus, the mechanical resonance frequency, ω_0, is only one-half that of the electromechanical frequency which is equal to the frequency of the free space photon, ω, which excites the vibrational mode of the hydrogen molecule or hydrogen molecular ion. The vibrational energy, E_{vib}, corresponding to the photon is given by

$$E_{vib} = \hbar\omega = \hbar\omega_0 = \hbar\sqrt{\frac{k}{\mu}} = 2kA^2 \tag{11.153}$$

where Planck's equation (Eq. (11.127)) was used. The reduced mass is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{11.154}$$

Thus,

$$A = \sqrt{\frac{\hbar\omega_0}{2k}} \tag{11.155}$$

Since the protons and electron are not fixed, but vibrate about the center of mass, the maximum amplitude is given by the reduced amplitude, $A_{reduced}$, given by

$$A_{reduced} = \frac{A_1 A_2}{A_1 + A_2} \tag{11.156}$$

where A_n is the amplitude n if the origin is fixed. Thus, Eq. (11.155) becomes

$$A_{reduced} = \frac{1}{2}\sqrt{\frac{\hbar\omega_0}{2k}} \tag{11.157}$$

and from Eq. (11.148), $A_{reduced}$ is

$$A_{reduced} = \frac{1}{2}\sqrt{\frac{\hbar\omega_0}{2k}} = \frac{1}{2}\sqrt{\frac{\hbar}{2k}}\left(\frac{k}{\mu}\right)^{1/4} = \frac{\sqrt{\hbar}}{2^{3/2}(k\mu)^{1/4}} \tag{11.158}$$

Then, from Eq. (11.67), $A_{c'}$, the displacement of c' is the eccentricity e given by Eq. (11.113) times $A_{reduced}$ (Eq. (11.158)):

$$A_{c'} = eA_{reduced} = \frac{A_{reduced}}{2} = \frac{\sqrt{\hbar}}{2^{5/2}(k\mu)^{1/4}} \tag{11.159}$$

Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the

corresponding frequency, $\omega(0)$, for a hydrogen-type molecular ion $H_2^+(1/p)$ given by Eqs. (11.136) and (11.145) is

$$\omega(0) = p^2\sqrt{\frac{k(0)}{\mu}} = p^2\sqrt{\frac{165.51\ Nm^{-1}}{\mu}} = p^2 4.449\ X\ 10^{14}\ radians/s \tag{11.160}$$

where the reduced nuclear mass of hydrogen given by Eq. (11.154) is

$$\mu = 0.5m_p \tag{11.161}$$

and the spring constant, $k(0)$, given by Eqs. (11.136) and (11.145) is

$$k(0) = p^4 165.51\ Nm^{-1} \tag{11.162}$$

The transition-state vibrational energy, $E_{vib}(0)$, is given by Planck's equation (Eq. (11.127)):

$$E_{vib}(0) = \hbar\omega = \hbar p^2 4.44865\ X\ 10^{14}\ rad/s = p^2 0.2928\ eV \tag{11.163}$$

The amplitude of the oscillation, $A_{reduced}(0)$, given by Eq. (11.158) and Eqs. (11.161-11.162) is

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 165.51\ Nm^{-1}\mu\right)^{1/4}} = \frac{5.952\ X\ 10^{-12}\ m}{p} = 0.1125\frac{a_o}{p} \tag{11.164}$$

Then, from Eq. (11.67), $A_{c'}(0)$, the displacement of c' is the eccentricity e given by Eq. (11.113) times $A_{reduced}(0)$ (Eq. (11.164)):

$$A_{c'}(0) = eA_{reduced}(0) = \frac{A_{reduced}(0)}{2} = \frac{\sqrt{\hbar}}{2^{5/2}(k\mu)^{1/4}} = \frac{0.05624a_o}{p} \tag{11.165}$$

The spring constant and vibrational frequency for the formed molecular ion are then obtained from Eqs. (11.136) and (11.141-11.145) using the increases in the semimajor axis and internuclear distances due to vibration in the transition state. The vibrational energy, $E_{vib}(1)$, for the $H_2^+(1/p)$ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by adding $A_{c'}(0)$ (Eq. (11.159)) to the distances a and $a + c'$ in Eqs. (11.145) and (11.163) is

$$E_{vib}(1) = p^2 0.270\ eV \tag{11.166}$$

where υ is the vibrational quantum number.

A harmonic oscillator is a linear system as given by Eq. (11.146). In this case, the predicted resonant vibrational frequencies and energies, spring constants, and amplitudes for $H_2^+(1/p)$ for vibrational transitions to higher energy $\upsilon_i \rightarrow \upsilon_f$ are given by $(\upsilon_f - \upsilon_i)$ times the corresponding parameters given by Eq. (11.160) and Eqs. (11.162-11.164). However,

excitation of vibration of the molecular ion by external radiation causes the semimajor axis and, consequently, the internuclear distance to increase as a function of the vibrational quantum number υ. Consequently, the vibrational energies of hydrogen-type molecular ions are nonlinear as a function of the vibrational quantum number υ. The lines become more closely spaced and the change in amplitude, $\Delta A_{reduced}$, between successive states becomes larger as higher states are excited due to the distortion of the molecular ion in these states. The energy difference of each successive transition of the vibrational spectrum can be obtained by considering nonlinear terms corresponding to anharmonicity.

The harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [14] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. The energy $\tilde{\nu}_\upsilon$ of state υ is

$$\tilde{\nu}_\upsilon = \upsilon\omega_0 - \upsilon(\upsilon-1)\omega_0 x_0, \quad \upsilon = 0,1,2,3... \tag{11.167}$$

where

$$\omega_0 x_0 = \frac{hc\omega_0^2}{4D_0} \tag{11.168}$$

ω_0 is the frequency of the $\upsilon = 1 \rightarrow \upsilon = 0$ transition corresponding to Eq. (11.166), and D_0 is the bond dissociation energy given by Eq. (11.198). From Eqs. (11.166), (11.168), and (11.198),

$$\omega_0 x_0 = \frac{100hc\left(8.06573X10^3 \ \frac{cm^{-1}}{eV} p^2 0.270 \ eV\right)^2}{4e\left(p^2 2.535 \ eV + p^3 0.118755 \ eV\right)} cm^{-1} \tag{11.169}$$

The vibrational energies of successive states are given by Eqs. (11.166-11.167) and (11.169).

Using Eqs. (11.145), (11.158-11.160), (11.162-11.169), and (11.199) the corresponding parameters for deuterium-type molecular ions with

$$\mu = m_p \tag{11.170}$$

are

$$\omega(0) = p^2\sqrt{\frac{k(0)}{\mu}} = p^2\sqrt{\frac{165.65 \ Nm^{-1}}{\mu}} = p^2 3.147 \ X \ 10^{14} \ radians/s \tag{11.171}$$

$$k(0) = p^4 165.65 \ Nm^{-1} \tag{11.172}$$

$$E_{vib}(0) = p^2 0.20714 \ eV \tag{11.173}$$

$$A_{reduced}(0)=\frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 165.65\ Nm^{-1}\mu\right)^{1/4}}=\frac{5.004\ X\ 10^{-12}\ m}{p}=0.09457\frac{a_o}{p} \tag{11.174}$$

$$E_{vib}(1)=p^2 0.193\ eV \tag{11.175}$$

$$\omega_0 x_0=\frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}p^2 0.193\ eV\right)^2}{4e\left(p^2 2.5770\ eV+p^3 0.118811\ eV\right)}cm^{-1} \tag{11.176}$$

The vibrational energies of successive states are given by Eqs. (11.167) and (11.175-11.176).

THE DOPPLER ENERGY TERM OF HYDROGEN-TYPE MOLECULAR IONS

As shown in the Vibration of Hydrogen-type Molecular Ions section, the electron orbiting the nuclei at the foci of an ellipse may be perturbed such that a stable reentrant orbit is established that gives rise to a vibrational state corresponding to time harmonic oscillation of the nuclei and electron. The perturbation is caused by a photon that is resonant with the frequency of oscillation of the nuclei wherein the radiation is electric dipole with the corresponding selection rules.

Oscillation may also occur in the transition state. The perturbation arises from the decrease in internuclear distance as the molecular bond forms. Relative to the unperturbed case given in the Force Balance of Hydrogen-type Molecular Ions section, the reentrant orbit may give rise to a decrease in the total energy while providing a transient kinetic energy to the vibrating nuclei. However, as an additional condition for stability, radiation must be considered. Regarding the potential for radiation, the nuclei may be considered point charges. A point charge undergoing periodic motion accelerates and as a consequence radiates according to the Larmor formula (cgs units) [15]:

$$P=\frac{2e^2}{3c^3}|\dot{\mathbf{v}}|^2 \tag{11.177}$$

where e is the charge, $\dot{\mathbf{v}}$ is its acceleration, and c is the speed of light. The radiation has a corresponding force that can be determined based on conservation of energy with radiation. The radiation reaction force, $\mathbf{F}_{rad}$, given by Jackson [16] is

$$\mathbf{F}_{rad}=\frac{2}{3}\frac{e^2}{c^3}\ddot{\mathbf{v}} \tag{11.178}$$

Then, the Abraham-Lorentz equation of motion is given by [16]

$$m\left(\dot{\mathbf{v}}-\frac{2}{3}\frac{e^2}{mc^3}\ddot{\mathbf{v}}\right)=\mathbf{F}_{ext} \tag{11.179}$$

where $\mathbf{F}_{ext}$ is the external force and m is the mass. The external force for the vibrating system is given by Eq. (11.146).

$$\mathbf{F}_{ext}=kx \tag{11.180}$$

where x is the displacement of the protons along the semimajor axis from the position of the initial foci of the stationary state in the absence of vibration with a reentrant orbit of the electron. A nonradiative state must be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied.

As shown in the Resonant Line Shape and Lamb Shift section, the spectroscopic linewidth arises from the classical rise-time band-width relationship, and the Lamb Shift is due to conservation of energy and linear momentum and arises from the radiation reaction force between the electron and the photon. The radiation reaction force in the case of the vibration of the molecular ion in the transition state corresponds to a Doppler energy, E_D, that is dependent on the motion of the electron and the nuclei. The Doppler energy of the electron is given by Eq. (2.146)

$$\overline{E}_D \cong 2\sqrt{E_K E_R}=E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} \tag{11.181}$$

where E_R is the recoil energy which arises from the photon's linear momentum given by Eq. (2.141), E_K is the vibrational kinetic energy of the reentrant orbit in the transition state, and M is the mass of the electron m_e.

As given in the Vibration of Hydrogen-Type Molecular Ions section, for inverse-squared central field, the coefficient of x in Eq. (11.135) is positive, and the equation is the same as that of the simple harmonic oscillator. Since the electron of the hydrogen molecular ion is perturbed as the internuclear separation decreases with bond formation, it oscillates harmonically about the semimajor axis given by Eq. (11.116), and an approximation of the angular frequency of this oscillation is

$$\omega=\sqrt{\frac{\left[\frac{-3}{a}f(a)-f'(a)\right]}{m_e}}=\sqrt{\frac{k}{m_e}} \tag{11.182}$$

From Eqs. (11.115), (11.117), and (11.119), the central force terms between the electron MO and the two protons are

$$f(a) = -\frac{2pe^2}{4\pi\varepsilon_o a^2} \tag{11.183}$$

and

$$f'(a) = \frac{4pe^2}{4\pi\varepsilon_o a^3} \tag{11.184}$$

Thus, the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{2pe^2}{4\pi\varepsilon_o\left(\frac{2a_H}{p}\right)^3}}{m_e}} = p^2 2.06538\, X\ 10^{16}\ rad/s \tag{11.185}$$

where the semimajor axis, a, is $a = \frac{2a_H}{p}$ according to Eq. (11.116) including the reduced electron mass. The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar p^2 2.06538\, X\ 10^{16}\ rad/s = p^2 13.594697\ eV \tag{11.186}$$

In Eq. (11.181), substitution of the total energy of the hydrogen molecular ion, E_T, (Eq. (11.125)) for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (11.186) for $\overline{E}_K$ gives the Doppler energy of the electron for the reentrant orbit.

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -p^2 16.28034\ eV\sqrt{\frac{2e\left(p^2 13.594697\ eV\right)}{m_e c^2}} = -p^3 0.118755\ eV \tag{11.187}$$

The total energy of the molecular ion is decreased by $\overline{E}_D$.

In addition to the electron, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency given in the Vibration of Hydrogen-Type Molecular Ions section. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [17]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of the molecular ion given by Eq. (11.166). The decrease in the energy of the hydrogen molecular ion due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electron and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ and $\overline{E}_{Kvib}$. Using Eq. (11.187) and E_{vib} from Eq. (11.166) gives

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar p^2\sqrt{\frac{k}{\mu}} \tag{11.188}$$

$$\overline{E}_{osc} = -p^3 0.118755\ eV + \frac{1}{2}p^2\left(0.29282\ eV\right) \tag{11.189}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies $\overline{E}_K$ are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies. Using Eq. (11.187) with the deuterium reduced electron mass for E_T and $\overline{E}_D$, and E_{vib} for $D_2^+(1/p)$ given by Eq. (11.173), that corresponds to the deuterium reduced nuclear mass (Eq. (11.170)), the corresponding $\overline{E}_{osc}$ is

$$\overline{E}_{osc} = -p^3 0.118811\ eV + \frac{1}{2}p^2\left(0.20714\ eV\right) \tag{11.190}$$

TOTAL, IONIZATION, AND BOND ENERGIES OF HYDROGEN AND DEUTERIUM MOLECULAR IONS

The total energy of the hydrogen molecular ion which is equivalent to the negative of the ionization energy is given by the sum of E_T (Eqs. (11.121) and (11.125)) and $\overline{E}_{osc}$ given by Eqs. (11.185-11.188). Thus, the total energy of the hydrogen molecular ion having a central field of $+pe$ at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_T = V_e + V_p + T + \overline{E}_{osc} \tag{11.191}$$

$$E_T = -p^2\left\{\frac{e^2}{8\pi\varepsilon_o a_H}(4\ln 3 - 1 - 2\ln 3)\left[1 + p\sqrt{\frac{2\hbar\sqrt{\frac{2e^2}{4\pi\varepsilon_o(2a_H)^3}}}{m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\} \tag{11.192}$$

$$= -p^2 16.2803\ eV - p^3 0.118811\ eV + \frac{1}{2}p^2\hbar\sqrt{\frac{k}{\mu}}$$

From Eqs. (11.189) and (11.191-11.192), the total energy for hydrogen-type molecular ions is

$$E_T = -p^2 16.28033\ eV + \bar{E}_{osc}$$
$$= -p^2 16.28033\ eV - p^3 0.118755\ eV + \frac{1}{2} p^2 (0.29282\ eV) \quad (11.193)$$
$$= -p^2 16.13392\ eV - p^3 0.118755\ eV$$

The total energy of the deuterium molecular ion is given by the sum of E_T (Eq. (11.125)) corrected for the reduced electron mass of D and $\bar{E}_{osc}$ given by Eq. (11.190):

$$E_T = -p^2 16.284\ eV + \bar{E}_{osc}$$
$$= -p^2 16.284\ eV - p^3 0.118811\ eV + \frac{1}{2} p^2 (0.20714\ eV) \quad (11.194)$$
$$= -p^2 16.180\ eV - p^3 0.118811\ eV$$

The bond dissociation energy, E_D, is the difference between the total energy of the corresponding hydrogen atom or $H(1/p)$ atom [18-19], called hydrino atom having a principal quantum number $1/p$ where p is an integer, and E_T.

$$E_D = E(H(1/p)) - E_T \quad (11.195)$$

where [18]

$$E(H(1/p)) = -p^2 13.59844\ eV \quad (11.196)$$

and [19]

$$E(D(1/p)) = -p^2 13.603\ eV \quad (11.197)$$

The hydrogen molecular ion bond energy, E_D, is given by Eq. (11.193) with the reduced electron mass and Eqs. (11.195-11.196):

$$E_D = -p^2 13.59844 - E_T$$
$$= -p^2 13.59844 - (-p^2 16.13392\ eV - p^3 0.118755\ eV) \quad (11.198)$$
$$= p^2 2.535\ eV + p^3 0.118755\ eV$$

The deuterium molecular ion bond energy, E_D, is given by Eq. (11.194) with the reduced electron mass of D and Eqs. (11.195) and (11.197):

$$E_D = -p^2 13.603 - E_T$$
$$= -p^2 13.603 - (-p^2 16.180\ eV - p^3 0.118811\ eV) \quad (11.199)$$
$$= p^2 2.5770\ eV + p^3 0.118811\ eV$$

HYDROGEN-TYPE MOLECULES

FORCE BALANCE OF HYDROGEN-TYPE MOLECULES

Hydrogen-type molecules comprise two indistinguishable electrons bound by an elliptic field. Each electron experiences a centrifugal force, and the balancing centripetal force (on each electron) is produced by the electric force between the electron and the elliptic electric field and the magnetic force between the two electrons causing the electrons to pair. In addition to nonradiation, the angular frequency given by Eq. (11.24) corresponds to a Lorentzian invariant magnetic moment of a Bohr magneton, μ_B, as given in the Magnetic Moment of an Ellipsoidal MO section. The internal field is uniform along the major axis, and the far field is that of a dipole as shown in the Magnetic Field of an Ellipsoidal MO section. The magnetic force is derived by first determining the interaction of the two electrons due to the field of the outer electron 2 acting on the magnetic moments of electron 1 and vice versa. Insight to the behavior is given by considering the physics of a single bound electron in an externally applied uniform magnetic field as discussed in the Two-Electron Atoms section. The orbitsphere-cvf and the uniform current- (charge-) density function $Y_0^0(\theta,\phi)$ was given in the Orbitsphere Equation of Motion for $\ell = 0$ section and Appendix III. The resultant angular momentum projections of the spherically-symmetric orbitsphere current density, $Y_0^0(\theta,\phi)$, are $\mathbf{L}_{xy} = \frac{\hbar}{4}$ and $\mathbf{L}_z = \frac{\hbar}{2}$. As shown in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section, the electron spin angular momentum gives rise to a trapped photon with $\hbar$ of angular momentum along an $\mathbf{S}$-axis. Then, the spin state of an orbitsphere comprises a photon standing wave that is phase-matched to a spherical harmonic source current, a spherical harmonic dipole $Y_\ell^m(\theta,\phi) = \sin\theta$ with respect to the $\mathbf{S}$-axis. The dipole spins about the $\mathbf{S}$-axis at the angular velocity given by Eq.(1.55) with $\hbar$ of angular momentum. $\mathbf{S}$ rotates about the z-axis at the Larmor frequency at $\theta = \frac{\pi}{3}$ such that it has a static projection of the angular momentum of $\mathbf{S}_\parallel = \pm\hbar\cos\frac{\pi}{3} = \pm\frac{\hbar}{2}\,\mathbf{i}_{Z_R}$ as given by Eq. (1.85), and from Eq. (1.84), the projection of $\mathbf{S}$ onto the transverse plane (xy-plane) is $\mathbf{S}_\perp = \hbar\sin\frac{\pi}{3} = \pm\sqrt{\frac{3}{4}}\hbar\,\mathbf{i}_{Y_R}$. Then, the vector projection of the radiation-reaction-type magnetic force of the Two Electron Atom section given by Eqs. (7.24)

and (7.31) contain the factor $\sqrt{\frac{3}{4}}\hbar$. This represents the maximum projection of the time-dependent magnetic moment onto an axis of the spherical-central-force system.

The orbitsphere can serve as a basis element to form a molecular orbital (MO). The total magnitude of the angular momentum of $\hbar$ is conserved for each member of the linear combinations of $Y_0^0(\theta,\phi)$'s in the transition from the $Y_0^0(\theta,\phi)$'s to the MO. Since the charge and current densities are equivalent by the ratio of the frequency, the solution of Laplace's equation for the charge density that is an equipotential energy surface also determines the current density. The frequency and the velocity are given by Newton's laws. Specifically, the further constraint from Newton's laws that the orbital surface is a constant total energy surface and the condition of nonradiation provide that the angular velocity of each point on the surface is constant, the current is continuous and constant, and determines the corresponding velocity function. In non-spherical coordinates, the nonuniform charge distribution given by Laplace's equation is compensated by a nonuniform velocity distribution such that the constant current condition is met. Then, the conservation of the angular momentum is provided by symmetrically stretching the current density along an axis perpendicular to the plane defined by the orthogonal components of angular momentum. The angular momentum projection may be determined by first considering the case of the hydrogen molecular ion. Specifically, the angular momentum must give the results of the Stern-Gerlach experiment as shown for atomic electrons and free electrons in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section and Stern-Gerlach Experiment section, respectively.

The hydrogen-molecular-ion MO, and all MOs in general, have cylindrical symmetry along the bond axis. Thus, for the hydrogen molecular ion, the two orthogonal semiminor axes are equivalent and interchangeable. Then, in general, $Y_0^0(\theta,\phi)$ can serve as a basis element for an MO having equal angular momentum projections along each of the semiminor axes. This defines the plane and the orthogonal axis for stretching the $Y_0^0(\theta,\phi)$ basis element to form the MO. Thus, to conserve angular momentum, $Y_0^0(\theta,\phi)$ is stretched along the semimajor axis as shown in Figure 2. This gives rise to an ellipsoidal surface comprised of the equivalent of elliptical-orbit, plane cross sections in the direction parallel to the semimajor axis with equal angular momentum projections along the orthogonal semiminor axes when the basis element has equal orthogonal angular momentum components.

As shown in the Exact Generation of $Y_0^0(\theta,\phi)$ from the Orbitsphere-cvf section, the orbitsphere is comprised of the uniform function $Y_0^0(\theta,\phi)$ corresponding to STEP ONE having the angular momentum components $\mathbf{L}_{xy}=0$ and $\mathbf{L}_z=\frac{\hbar}{4}$ and the uniform function $Y_0^0(\theta,\phi)$ corresponding to STEP TWO having the angular momentum components $\mathbf{L}_{xy}=\frac{\hbar}{4}$ and $\mathbf{L}_z=\frac{\hbar}{4}$. These components are separable. Then, the basis element $Y_0^0(\theta,\phi)$ for the construction of an MO that conserves the total magnitude of the angular momentum of $\hbar$ (Eq. (1.57)) that matches the MO conditions of equal orthogonal components of angular momentum along each semiminor axis is a single $Y_0^0(\theta,\phi)$ that is generated according to STEP TWO but with twice the angular momentum in each great-circle basis element to give $\mathbf{L}_{xy}=\frac{\hbar}{2}$ and $\mathbf{L}_z=\frac{\hbar}{2}$.

Now consider the behavior of the hydrogen molecular ion in a magnetic field. As shown in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section, the photon angular momentum corresponding to the resonant excitation of the Larmor excited state is $\hbar$, and the angular momentum change corresponding to the spin-flip transition is also $\hbar$. Furthermore, torque balance for the orbitsphere was determined by considering the energy minimum due to the interaction of the magnetic moments corresponding to the components of angular momentum. In the case of the hydrogen molecular ion, the Larmor-excitation photon carries $\hbar$ of angular momentum that gives rise to a prolate spheroidal dipole current about an $\mathbf{S}$-axis in the same manner as in the case of the spherical dipole of the Larmor excited orbitsphere shown in Figures 1.15 and 1.16 in Chapter 1. The former are given by the prolate angular function, which comprises an associated Legendre function $P_\ell^m(\eta)$ [20], and the latter comprises the spherical harmonic dipole $Y_\ell^m(\theta,\phi)=\sin\theta$. Both are with respect to the $\mathbf{S}$-axis. For hydrogen molecular ion, $\frac{\hbar}{2}$ of intrinsic spin is along each of the semiminor axes of the prolate spheroidal MO. Torque balance is achieved with $\mathbf{S}$ along the semimajor axis as shown in Figure 3. Thus, the Larmor excitation is along the semimajor axis. In general, all bonds are cylindrically symmetrical about the internuclear or semimajor axis; thus, the Larmor precession occurs about the bond

axis of an MO wherein the intrinsic angular momentum components rotate about **S** at the Larmor frequency.

In the coordinate system rotating at the Larmor frequency (denoted by the axes labeled X_R, Y_R, and Z_R in Figure 2), the angular momentum of **S** of magnitude $\hbar$ is stationary. The Y_R-component of magnitude $\frac{\hbar}{2}$ and the Z_R-component of magnitude $\frac{\hbar}{2}$ rotate about **S** at the Larmor frequency. The rotation occurs due to a resonant excitation that results in a balance between the magnetic moment of **S** of μ_B corresponding to its angular momentum of $\hbar$ (Eq. (28) of Box 1.3 and Eq. (2.65)) and those of the orthogonal $\frac{\hbar}{2}$ angular momentum components along Z_R and Y_R of $\frac{\mu_B}{2}$.

Then, the **S**-axis is the direction of the magnetic moment of each unpaired electron of a molecule or molecular ion. The magnetic moment of **S** of μ_B corresponding to its $\hbar$ of angular momentum is consistent with the Stern-Gerlach experiment wherein the Larmor excitation can only be parallel or antiparallel to the magnetic field in order to conserve the angular momentum of the electron, the photon corresponding to the Larmor excitation, and the $\hbar$ of angular momentum of the photon that causes a 180° flip of the direction of **S**. The result is the same as that for the atomic electron and the free electron given in the Resonant Precession of the Spin-1/2-Current-Density Function Gives Rise to the Bohr Magneton section and Stern-Gerlach Experiment section, respectively. The magnetic field is given in the Magnetic Field of an Ellipsoidal Molecular Orbital section.

Next, consider the magnetic-pairing force of the hydrogen molecule due to the spin-angular-momentum components. The magnetic moments of electrons 1 and 2 of the hydrogen molecule cancel as they are spin paired to form an energy minimum at the radius (i.e. $r_1 = r_2$). The magnetic force follows the derivation for that between the electrons of two-electron atoms as given in the Two-Electron Atoms section. The latter force was derived by first determining the interaction of the two electrons due to the field of the outer electron 2 acting on the magnetic moments of electron 1 and vice versa. It was also given by the relationship between the angular momentum, energy, and frequency for the transition of electron 2 from the continuum to the ground state. The magnitude of the magnetic force given by Eqs. (7.24) and (7.31) is equivalent to that of the centrifugal force given by Eqs.

(7.1-7.2) multiplied by $\frac{1}{Z\hbar}$ times the magnitude of the photon angular momentum vector that precesses at the Larmor frequency given by Eq. (7.4). In the present case of hydrogen-type molecules, the radiation-reaction-type magnetic force arises between the electrons, each having the components shown in Figure 3. With the photon angular momentum projection of $\hbar$ and the total nuclear (non-photon-field) of 2, the magnitude of the magnetic force between the two electrons is 1/2 that of the centrifugal force given by Eq. (11.95).

The hydrogen-type molecule is formed by the binding of an electron 2 to the hydrogen-type molecular ion comprising two protons at the foci of the prolate spheroidal MO of electron 1. The ellipsoids of electron 1 and electron 2 are confocal; thus, the electric fields and the corresponding forces are normal to the each MO of electron 1 and electron 2. The two electrons are bound by the central field of the two protons as in the case of the molecular ion. Since the field of the protons is only ellipsoidal on average, the field of the hydrogen-type molecular ion is not equivalent to an ellipsoid of charge +1 outside of the electron MO. In addition there is a spin pairing force between the two electrons. Due to the force between electron 2 and electron 1 as well as the central force of the protons, the balance between the centrifugal force and the central field of electron 2 of the hydrogen-type molecule formed by electron 2 binding to a hydrogen-type molecular ion also given by Eq. (11.115). The force balance between the centrifugal force and the sum of the Coulombic and magnetic spin-pairing forces to solve for the semimajor axis is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\varepsilon_o a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{11.200}$$

$$\frac{2a_o}{pa} - \frac{a_o}{pa} = 1 \tag{11.201}$$

$$a = \frac{a_o}{p} \tag{11.202}$$

Substitution of Eq. (11.202) into Eq. (11.79) is

$$c' = \frac{1}{p\sqrt{2}} a_o \tag{11.203}$$

The internuclear distance given by multiplying Eq. (11.203) by two is

$$2c' = \frac{a_o\sqrt{2}}{p} \tag{11.204}$$

Substitution of Eqs. (11.202-11.203) into Eq. (11.80) is

$$b = c = \frac{1}{p\sqrt{2}} a_o \tag{11.205}$$

Substitution of Eqs. (11.202-11.203) into Eq. (11.67) is

$$e = \frac{1}{\sqrt{2}} \tag{11.206}$$

For hydrogen, $r(t) = D$ for $\theta = n\frac{\pi}{2}$, $n = 0,1,2,3,4$. Thus, there is no dipole moment and the molecule is not predicted to be infrared active. However, it is predicted to be Raman active due to the quadrupole moment. The liquefaction temperature of H_2 is also predicted to be significantly higher than isoelectronic helium.

ENERGIES OF HYDROGEN-TYPE MOLECULES

The energy components defined previously for the molecular ion, Eqs. (11.117), (11.119), (11.120), and (11.121), apply in the case of the corresponding molecule except that all of the field lines of the protons must end on the MO comprising two-paired electrons. With spin pairing of the mirror-image-current electrons, the scaling factors due to the non-ellipsoidal variation of the electric field of the protons is unity as in the case of the sum of squares of spherical harmonics. Thus, the hydrogen-type molecular energies are given by the integral of the forces without correction. Then, each molecular-energy component is given by the integral of corresponding force in Eq. (11.200) where each energy component is the total for the two equivalent electrons with the central-force action at the position of the electron MO where the parameters a and b are given by Eqs. (11.202) and (11.205), respectively.

The potential energy, V_e, of the two-electron MO comprising equivalent electrons in the field of magnitude p times that of the two protons at the foci is

$$\begin{aligned} V_e &= 2\frac{-pe^2}{4\pi\varepsilon_o} D \frac{ab^2}{2D} \int_{\xi}^{\infty} \frac{d\xi}{R_\xi} \\ &= \frac{-2pe^2}{8\pi\varepsilon_o} \int_{\xi}^{\infty} \frac{d\xi}{(\xi + b)\sqrt{\xi + a}} \\ &= \frac{-2pe^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \end{aligned} \tag{11.207}$$

which is equivalent to $Ze = 2pe$ times the potential of the MO given by Eq. (11.46) after Eq. (11.114). The potential energy, V_p, due to proton-proton repulsion in the field of magnitude p times that of the protons at the foci ($\xi = 0$) is

$$V_p = \frac{p}{8\pi\varepsilon_o}\frac{e^2}{\sqrt{a^2-b^2}} \tag{11.208}$$

The kinetic energy, T, of the two-electron MO of total mass $2m_e$ is

$$\begin{aligned} T &= 2\frac{-\hbar^2}{2m_e a^2 b^2} D \frac{ab^2}{2D}\int_{\xi}^{\infty}\frac{d\xi}{R_\xi} \\ &= \frac{-\hbar^2}{2m_e a}\int_{\xi}^{\infty}\frac{d\xi}{(\xi+b)\sqrt{\xi+a}} \\ &= \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \end{aligned} \tag{11.209}$$

The magnetic energy, V_m, of the two-electron MO of total mass $2m_e$ corresponding to the magnetic force of Eq. (11.200) is

$$\begin{aligned} V_m &= 2\frac{-\hbar^2}{2(2m_e)a^2 b^2} D \frac{ab^2}{2D}\int_{\xi}^{\infty}\frac{d\xi}{R_\xi} \\ &= \frac{-\hbar^2}{4m_e a}\int_{\xi}^{\infty}\frac{d\xi}{(\xi+b)\sqrt{\xi+a}} \\ &= \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \end{aligned} \tag{11.210}$$

The total energy, E_T, is given by the sum of the energy terms (Eqs. (11.207-11.210)):

$$E_T = V_e + T + V_m + V_p \tag{11.211}$$

$$E_T = -13.60\ eV\left[\left(2p^2\sqrt{2} - p^2\sqrt{2} + \frac{p^2\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - p^2\sqrt{2}\right] = -p^2 31.63 \tag{11.212}$$

where a and b are given by Eqs. (11.202) and (11.205), respectively. The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical mechanics equation of an ellipse that considered only the binding force between the protons and the electrons and the electron centrifugal force. As shown by Eqs. (11.290) and (11.292), T is one-half the magnitude of V_e as required for an inverse-squared force [1] wherein V_e is the source of T.

VIBRATION OF HYDROGEN-TYPE MOLECULES

The vibrational energy levels of hydrogen-type molecules may be solved in the same manner as hydrogen-type molecular ions given in the Vibration of Hydrogen-type Molecular Ions section. The corresponding central force terms of Eq. (11.136) are

$$f(a)=-\frac{pe^2}{8\pi\varepsilon_o a^2} \tag{11.213}$$

and

$$f'(a)=\frac{pe^2}{4\pi\varepsilon_o a^3} \tag{11.214}$$

The distance for the reactive nuclear-repulsive terms is given by the sum of the semimajor axis, a, and c', 1/2 the internuclear distance. The contribution from the repulsive force between the two protons is

$$f(a+c')=\frac{pe^2}{8\pi\varepsilon_o (a+c')^2} \tag{11.215}$$

and

$$f'(a+c')=-\frac{pe^2}{4\pi\varepsilon_o (a+c')^3} \tag{11.216}$$

Thus, from Eqs. (11.136) and (11.213-11.216), the angular frequency of the oscillation is

$$\omega=\sqrt{\frac{\frac{pe^2}{8\pi\varepsilon_o a^3}-\frac{pe^2}{8\pi\varepsilon_o (a+c')^3}}{\mu}}=\sqrt{\frac{\frac{pe^2}{8\pi\varepsilon_o \left(\frac{a_0}{p}\right)^3}-\frac{pe^2}{8\pi\varepsilon_o \left(\frac{\left(1+\frac{1}{\sqrt{2}}\right)a_0}{p}\right)^3}}{\mu}}=p^2 8.62385\,X\,10^{14}\ rad/s \tag{11.217}$$

where the semimajor axis, a, is $a=\frac{a_0}{p}$ according to Eq. (11.202) and c' is $c'=\frac{a_0}{p\sqrt{2}}$ according to Eq. (11.203). Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for a hydrogen-type molecule $H_2(1/p)$ given by Eqs. (11.136) and (11.145) is

$$\omega(0)=p^2\sqrt{\frac{k(0)}{\mu}}=p^2\sqrt{\frac{621.98\ Nm^{-1}}{\mu}}=p^2 8.62385\,X\,10^{14}\ radians/s \tag{11.218}$$

where the reduced nuclear mass of hydrogen is given by Eq. (11.161) and the spring constant, $k(0)$, given by Eqs. (11.136) and (11.217) is

$$k(0)=p^4 621.98\ Nm^{-1} \tag{11.219}$$

The transition-state vibrational energy, $E_{vib}(0)$, is given by Planck's equation (Eq. (11.127)):

$$E_{vib}(0) = \hbar\omega = \hbar p^2 8.62385\ X\ 10^{14}\ rad/s = p^2 0.56764\ eV \tag{11.220}$$

The amplitude of oscillation, $A_{reduced}(0)$, given by Eqs. (11.158), (11.161), and (11.219) is

$$A_{reduced}(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 621.98\ Nm^{-1}\mu\right)^{1/4}} = \frac{4.275\ X\ 10^{-12}\ m}{p} = 0.08079\frac{a_o}{p} \tag{11.221}$$

Then, from Eq. (11.67), $A_{c'}(0)$, the displacement of c' is the eccentricity e given by Eq. (11.206) times $A_{reduced}(0)$ (Eq. (11.221)):

$$A_{c'}(0) = eA_{reduced}(0) = \frac{A_{reduced}(0)}{\sqrt{2}} = \frac{\sqrt{\hbar}}{4(k\mu)^{1/4}} = \frac{0.05713a_o}{p} \tag{11.222}$$

The spring constant and vibrational frequency for the formed molecule are then obtained from Eqs. (11.136) and (11.213-11.222) using the increases in the semimajor axis and internuclear distances due to vibration in the transition state. The vibrational energy, $E_{vib}(1)$, for the $H_2(1/p)$ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by adding $A_{c'}(0)$ (Eq. (11.222)) to the distances a and $a + c'$ in Eqs. (11.213-11.220) is

$$E_{vib}(1) = p^2 0.517\ eV \tag{11.223}$$

where υ is the vibrational quantum number. Using Eq. (11.176) with Eqs. (11.223) and (11.252), the anharmonic perturbation term, $\omega_0 x_0$, of $H_2(1/p)$ is

$$\omega_0 x_0 = \frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}\ p^2 0.517\ eV\right)^2}{4e\left(p^2 4.151\ eV + p^3 0.326469\ eV\right)} cm^{-1} \tag{11.224}$$

where ω_0 is the frequency of the $\upsilon = 1 \rightarrow \upsilon = 0$ transition corresponding to Eq. (11.223) and D_0 is the bond dissociation energy given by Eq. (11.252). The vibrational energies of successive states are given by Eqs. (11.167) and (11.223-11.224).

Using the reduced nuclear mass given by Eq. (11.170), the corresponding parameters for deuterium-type molecules $D_2(1/p)$ (Eqs. (11.213-11.224) and (11.253)) are

$$\omega(0) = p^2\sqrt{\frac{k(0)}{\mu}} = p^2\sqrt{\frac{621.98\ Nm^{-1}}{\mu}} = p^2 6.09798\ X\ 10^{14}\ radians/s \tag{11.225}$$

$$k(0) = p^4 621.98\ Nm^{-1} \tag{11.226}$$

$$E_{vib}(0) = p^2 0.4014\ eV \tag{11.227}$$

$$A_{reduced}(0)=\frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 621.98\ Nm^{-1}\mu\right)^{1/4}}=\frac{3.595\ X\ 10^{-12}\ m}{p}=0.06794\frac{a_o}{p} \tag{11.228}$$

$$E_{vib}(1)=p^2 0.371\ eV \tag{11.229}$$

$$\omega_0 x_0=\frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}p^2 0.371\ eV\right)^2}{4e\left(p^2 4.229\ eV+p^3 0.326469\ eV\right)}cm^{-1} \tag{11.230}$$

The vibrational energies of successive states are given by Eqs. (11.167) and (11.229-11.230).

THE DOPPLER ENERGY TERM OF HYDROGEN-TYPE MOLECULES

The radiation reaction force in the case of the vibration of the molecule in the transition state also corresponds to the Doppler energy, E_D, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. Here, a nonradiative state must also be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. Typically, a third body is required to form hydrogen-type molecules. For example, the exothermic chemical reaction of $H+H$ to form H_2 does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, M, to remove the bond energy—$H+H+M\rightarrow H_2+M^*$ [21]. The third body distributes the energy from the exothermic reaction, and the end result is the H_2 molecule and an increase in the temperature of the system. Thus, a third body removes the energy corresponding to the additional force term given by Eq. (11.180). From Eqs. (11.200), (11.207) and (11.209), the central force terms between the electron MO and the two protons are

$$f(a)=-\frac{pe^2}{4\pi\varepsilon_o a^2} \tag{11.231}$$

and

$$f'(a)=\frac{2pe^2}{4\pi\varepsilon_o a^3} \tag{11.232}$$

Thus, the angular frequency of this oscillation is

$$\omega=\sqrt{\frac{\frac{pe^2}{4\pi\varepsilon_o\left(\frac{a_0}{p}\right)^3}}{m_e}}=p^2 4.13414\ X\ 10^{16}\ rad/s \tag{11.233}$$

where the semimajor axis, a, is $a=\frac{a_0}{p}$ according to Eq. (11.202). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar p^2 4.13414\ X\ 10^{16}\ rad/s = p^2 27.2116\ eV \tag{11.234}$$

In Eq. (11.181), substitution of the total energy of the hydrogen molecule, E_T, (Eq. (11.212)) for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (11.234) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit.

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.635p^2\ eV\sqrt{\frac{2e\left(p^2 27.216\ eV\right)}{m_e c^2}} = -p^3 0.326469\ eV \tag{11.235}$$

The total energy of the molecule is decreased by $\overline{E}_D$.

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency given in the Vibration of Hydrogen-Type Molecules section. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [17]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of the molecule given by Eq. (11.148). The decrease in the energy of the hydrogen molecule due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ and $\overline{E}_{Kvib}$. Using Eq. (11.235) and E_{vib} from Eq. (11.220) gives

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar p^2\sqrt{\frac{k}{\mu}} \tag{11.236}$$

$$\overline{E}_{osc} = -p^3 0.326469\ eV + \frac{1}{2}p^2\left(0.56764\ eV\right) \tag{11.237}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies, $\overline{E}_K$, are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies. Using Eq. (11.235) and E_{vib} for $D_2\left(1/p\right)$ given by Eq. (11.227), that corresponds to the deuterium reduced nuclear mass (Eq. (11.170)), the corresponding $\overline{E}_{osc}$ is

$$\overline{E}_{osc} = -p^3 0.326469\ eV + \frac{1}{2}p^2\left(0.401380\ eV\right) \tag{11.238}$$

TOTAL, IONIZATION, AND BOND ENERGIES OF HYDROGEN AND DEUTERIUM MOLECULES

The total energy of the hydrogen molecule is given by the sum of E_T (Eqs. (11.211-11.212)) and $\overline{E}_{osc}$ given Eqs. (11.233-11.236). Thus, the total energy of the hydrogen molecule having a central field of $+pe$ at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc} \tag{11.239}$$

$$\begin{aligned} E_T &= -p^2 \left\{ \frac{e^2}{8\pi\varepsilon_o a_0} \left[\left(2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] \left[1 + p \sqrt{\frac{2\hbar \sqrt{\frac{e^2}{4\pi\varepsilon_o a_0^3}}}{m_e c^2}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\} \\ &= -p^2 31.635\ eV - p^3 0.326469\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{11.240}$$

From Eqs. (11.237) and (11.239-11.240), the total energy for hydrogen-type molecules is

$$\begin{aligned} E_T &= -p^2 31.635\ eV + \overline{E}_{osc} \\ &= -p^2 31.635\ eV - p^3 0.326469\ eV + \frac{1}{2} p^2 (0.56764\ eV) \\ &= -p^2 31.351\ eV - p^3 0.326469\ eV \end{aligned} \tag{11.241}$$

The total energy of the deuterium molecule is given by the sum of E_T (Eq. (11.212)) and $\overline{E}_{osc}$ given by Eq. (11.238):

$$\begin{aligned} E_T &= -p^2 31.6354\ eV + \overline{E}_{osc} \\ &= -p^2 31.6354\ eV - p^3 0.326469\ eV + \frac{1}{2} p^2 (0.401380\ eV) \\ &= -p^2 31.4345\ eV - p^3 0.326469\ eV \end{aligned} \tag{11.242}$$

The total energy, which includes the proton-proton-repulsion term is negative which justifies the original treatment of the force balance using the analytical mechanics equation of an ellipse that considered only the binding force between the protons and the electrons, the spin-pairing force, and the electron centrifugal force.

The first ionization energy of the hydrogen molecule, IP_1,

$$H_2(1/p) \rightarrow H_2^+(1/p) + e^- \tag{11.243}$$

is given by the difference of Eqs. (11.193) and (11.241):

$$\begin{aligned} IP_1 &= E_T\left(H_2^+(1/p)\right) - E_T\left(H_2(1/p)\right) \\ &= -p^2 16.13392\ eV - p^3 0.118755\ eV - \left(-p^2 31.351\ eV - p^3 0.326469\ eV\right) \\ &= p^2 15.2171\ eV + p^3 0.207714\ eV \end{aligned} \tag{11.244}$$

The second ionization energy, IP_2, is given by the negative of Eq. (11.193).

$$IP_2 = p^2 16.13392\ eV + p^3 0.118755\ eV \tag{11.245}$$

The first ionization energy of the deuterium molecule, IP_1,

$$D_2(1/p) \rightarrow D_2^+(1/p) + e^- \tag{11.246}$$

is given by the difference of Eqs. (11.194) and (11.242):

$$\begin{aligned} IP_1 &= E_T\left(D_2^+(1/p)\right) - E_T\left(D_2(1/p)\right) \\ &= -p^2 16.180\ eV - p^3 0.118811\ eV - \left(-p^2 31.4345\ eV - p^3 0.326469\ eV\right) \\ &= p^2 15.255\ eV + p^3 0.2077\ eV \end{aligned} \tag{11.247}$$

The second ionization energy, IP_2, is given by the negative of Eq. (11.194).

$$IP_2 = p^2 16.180\ eV + p^3 0.118811\ eV \tag{11.248}$$

The bond dissociation energy, E_D, is the difference between the total energy of the corresponding hydrogen atoms and E_T

$$E_D = E(2H(1/p)) - E_T \tag{11.249}$$

where [18]

$$E(2H(1/p)) = -p^2 27.20\ eV \tag{11.250}$$

and [19]

$$E(2D(1/p)) = -p^2 27.206\ eV \tag{11.251}$$

The hydrogen bond energy, E_D, is given by Eqs. (11.249-11.250) and (11.241):

$$\begin{aligned} E_D &= -p^2 27.20\ eV - E_T \\ &= -p^2 27.20\ eV - \left(-p^2 31.351\ eV - p^3 0.326469\ eV\right) \\ &= p^2 4.151\ eV + p^3 0.326469\ eV \end{aligned} \tag{11.252}$$

The deuterium bond energy, E_D, is given by Eqs. (11.249), (11.251), and (11.242):

$$\begin{aligned} E_D &= -p^2 27.206\ eV - E_T \\ &= -p^2 27.206\ eV - \left(-p^2 31.4345\ eV - p^3 0.326469\ eV\right) \\ &= p^2 4.229\ eV + p^3 0.326469\ eV \end{aligned} \tag{11.253}$$

THE HYDROGEN MOLECULAR ION $H_2[2c' = 2a_o]^+$

FORCE BALANCE OF HYDROGEN MOLECULAR ION

Force balance between the electric and centrifugal forces is given by Eq. (11.115) where $p = 1$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_o a b^2} D \tag{11.254}$$

which has the parametric solution given by Eq. (11.83) when

$$a = 2a_o \tag{11.255}$$

The semimajor axis, a, is also given by Eq. (11.116) where $p = 1$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.111) where $p = 1$.

$$2c' = 2a_o \tag{11.256}$$

The experimental internuclear distance is $2a_o$. The semiminor axis is given by Eq. (11.112) where $p = 1$.

$$b = \sqrt{3} a_o \tag{11.257}$$

The eccentricity, e, is given by Eq. (11.113).

$$e = \frac{1}{2} \tag{11.258}$$

ENERGIES OF THE HYDROGEN MOLECULAR ION

The potential energy, V_e, of the electron MO in the field of the protons at the foci ($\xi = 0$) is given by Eq. (11.117) where $p = 1$

$$V_e = \frac{-4e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \tag{11.259}$$

The potential energy, V_p, due to proton-proton repulsion is given by Eq. (11.120) where $p = 1$

$$V_p = \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} \tag{11.260}$$

The kinetic energy, T, of the electron MO is given by Eq. (11.119) where $p=1$

$$T = \frac{2\hbar^2}{m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.261}$$

Substitution of a and b given by Eqs. (11.255) and (11.257), respectively, into Eqs. (11.259-11.261) is

$$V_e = \frac{-4e^2}{8\pi\varepsilon_o a_H}\ln 3 = -59.7575\ eV \tag{11.262}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_o a_H} = 13.5984\ eV \tag{11.263}$$

$$T = \frac{2e^2}{8\pi\varepsilon_o a_H}\ln 3 = 29.8787\ eV \tag{11.264}$$

The Doppler term, $\overline{E}_{osc}$, for hydrogen and deuterium are given by Eqs. (11.189) and (11.190), respectively, where $p=1$

$$\overline{E}_{osc}\left(H_2^+\right) = \overline{E}_D + \overline{E}_{Kvib} = -0.118755\ eV + \frac{1}{2}(0.29282\ eV) = 0.027655 \tag{11.265}$$

$$\overline{E}_{osc}\left(D_2^+\right) = -0.118811\ eV + \frac{1}{2}(0.20714\ eV) = -0.01524\ eV \tag{11.266}$$

The total energy, E_T, for the hydrogen molecular ion given by Eqs. (11.191-11.193) is

$$\begin{aligned} E_T &= -\left\{\frac{e^2}{8\pi e_o a_H}(4\ln 3 - 1 - 2\ln 3)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{2e^2}{4\pi e_o (2a_H)^3}}{m_e}}{m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{m}}\right\} \\ &= -16.2803\ eV - 0.118811\ eV + \frac{1}{2}(0.29282\ eV) \\ &= -16.2527\ eV \end{aligned} \tag{11.267}$$

where in Eqs. (11.262-11.267), the radius of the hydrogen atom a_H (Eq. (1.287)) was used in place of a_0 to account for the corresponding electrodynamic force between the electron and the nuclei as given in the case of the hydrogen atom by Eq. (1.231). The negative of Eq. (11.267) is the ionization energy of H_2^+ and the second ionization energy, IP_2, of H_2. From

Eqs. (11.191-11.192) and (11.194), the total energy, E_T, for the deuterium molecular ion (the ionization energy of D_2^+ and the second ionization energy, IP_2, of D_2) is

$$E_T = -16.284\ eV - 0.118811\ eV + \frac{1}{2}(0.20714\ eV) = -16.299\ eV \tag{11.268}$$

The bond dissociation energy, E_D, is the difference between the total energy of the corresponding hydrogen atom and E_T. The hydrogen molecular ion bond energy, E_D, including the reduced electron mass given by Eq. (11.198) where $p = 1$ is

$$E_D = 2.535\ eV + 0.118755\ eV = 2.654\ eV \tag{11.269}$$

The experimental bond energy of the hydrogen molecular ion [22] is

$$E_D = 2.651\ eV \tag{11.270}$$

From Eq. (11.199) where $p = 1$, the deuterium molecular ion bond energy, E_D, including the reduced electron mass of D is

$$E_D = 2.5770\ eV + 0.118811\ eV = 2.6958\ eV \tag{11.271}$$

The experimental bond energy of the deuterium molecular ion [23] is

$$E_D = 2.691\ eV \tag{11.272}$$

VIBRATION OF THE HYDROGEN MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for H_2^+ given by Eq. (11.160) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{165.51\ Nm^{-1}}{\mu}} = 4.449\ X\ 10^{14}\ radians/s \tag{11.273}$$

wherein $p = 1$. The spring constant, $k(0)$, for H_2^+ given by Eq. (11.162) is

$$k(0) = 165.51\ Nm^{-1} \tag{11.274}$$

The vibrational energy, $E_{vib}(0)$, of H_2^+ during bond formation given by Eq. (11.163) is

$$E_{vib}(0) = 0.29282\ eV \tag{11.275}$$

The amplitude of oscillation given by Eq. (11.164) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(165.51\ Nm^{-1}\mu\right)^{1/4}} = 5.952\ X\ 10^{-12}\ m = 0.1125 a_o \tag{11.276}$$

The vibrational energy for the H_2^+ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by Eq. (11.166) is

$$E_{vib}(1) = 0.270\ eV \tag{11.277}$$

The experimental vibrational energy of H_2^+ [14, 19] is

$$E_{vib} = 0.271\ eV \tag{11.278}$$

The anharmonicity term of H_2^+ given by Eq. (11.169) is

$$\omega_0 x_0 = 55.39\ cm^{-1} \tag{11.279}$$

The experimental anharmonicity term of H_2^+ from NIST [19] is

$$\omega_e x_e = 66.2\ cm^{-1} \tag{11.280}$$

The vibrational energy for the D_2^+ $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by Eq. (11.175) is

$$E_{vib} = 0.193\ eV \tag{11.281}$$

The vibrational energy of the D_2^+ [19] based on calculations from experimental data is

$$E_{vib} = 0.196\ eV \tag{11.282}$$

The anharmonicity term of D_2^+ given by Eq. (11.176) is

$$\omega_0 x_0 = 27.86\ cm^{-1} \tag{11.283}$$

The experimental anharmonicity term of D_2^+ for the state $X\ {}^2\sum_g{}^{+1}s\sigma$ is not given, but the term for state $B\ {}^2\sum_g{}^{+3}d\sigma$ from NIST [19] is

$$\omega_e x_e = 2.62\ cm^{-1} \tag{11.284}$$

THE HYDROGEN MOLECULE $\mathbf{H_2}\left[\mathbf{2c' = \sqrt{2}a_o}\right]$

FORCE BALANCE OF THE HYDROGEN MOLECULE

The force balance equation for the hydrogen molecule is given by Eq. (11.200) where $p = 1$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_o a b^2} D + \frac{\hbar^2}{2 m_e a^2 b^2} D \tag{11.285}$$

which has the parametric solution given by Eq. (11.83) when

$$a = a_o \tag{11.286}$$

The semimajor axis, a, is also given by Eq. (11.202) where $p = 1$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.204) where $p = 1$.

$$2c' = \sqrt{2}a_o \tag{11.287}$$

The experimental internuclear distance is $\sqrt{2}a_o$. The semiminor axis is given by Eq. (11.205) where $p = 1$.

$$b = \frac{1}{\sqrt{2}}a_o \tag{11.288}$$

The eccentricity, e, is given by Eq. (11.206).

$$e = \frac{1}{\sqrt{2}} \tag{11.289}$$

The finite dimensions of the hydrogen molecule are evident in the plateau of the resistivity versus pressure curve of metallic hydrogen [24].

ENERGIES OF THE HYDROGEN MOLECULE

The energies of the hydrogen molecule are given by Eqs. (11.207-11.210) where $p = 1$

$$V_e = \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -67.8358\ eV \tag{11.290}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} = 19.2415\ eV \tag{11.291}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 33.9179\ eV \tag{11.292}$$

The energy, V_m, of the magnetic force is

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.9589\ eV \tag{11.293}$$

The Doppler terms, $\overline{E}_{osc}$, for hydrogen and deuterium molecules are given by Eqs. (11.237) and (11.238), respectively, where $p = 1$

$$\overline{E}_{osc}(H_2) = \overline{E}_D + \overline{E}_{Kvib} = -0.326469\ eV + \frac{1}{2}(0.56764\ eV) = -0.042649\ eV \tag{11.294}$$

$$\overline{E}_{osc}(D_2) = -0.326469\ eV + \frac{1}{2}(0.401380\ eV) = -0.125779\ eV \tag{11.295}$$

The total energy, E_T, for the hydrogen molecule given by Eqs. (11.239-11.241) is

$$E_T = -\left\{ \frac{e^2}{8\pi\varepsilon_o a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o a_0^3}}}{m_e c^2}}\right]-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

$$= -31.635\ eV - 0.326469\ eV + \frac{1}{2}(0.56764\ eV) \qquad (11.29$$

$$= -31.6776\ eV$$

6)

From Eqs. (11.239-11.240) and (11.242), the total energy, E_T, for the deuterium molecule is

$$E_T = -31.635\ eV - 0.326469\ eV + \frac{1}{2}(0.401380\ eV) = -31.7608\ eV \qquad (11.297)$$

The first ionization energies of the hydrogen and deuterium molecules, IP_1, (Eqs. (11.243) and (11.246)) are given by the differences in the total energy of corresponding molecular ions and molecules which are given by Eqs. (11.244) and (11.247), respectively, where $p=1$:

$$IP_1(H_2) = 15.2171\ eV + 0.207714\ eV = 15.4248\ eV \qquad (11.298)$$

$$IP_1(D_2) = 15.255\ eV + 0.2077\ eV = 15.4627\ eV \qquad (11.299)$$

The bond dissociation energy, E_D, is the difference between the total energy of two of the corresponding hydrogen atoms and E_T. The hydrogen molecular bond energy, E_D, given by Eq. (11.252) where $p=1$ is

$$E_D = 4.151\ eV + 0.326469\ eV = 4.478\ eV \qquad (11.300)$$

The experimental bond energy of the hydrogen molecule [22] is

$$E_D = 4.478\ eV \qquad (11.301)$$

The deuterium molecular bond energy, E_D, given by Eq. (11.253) where $p=1$ is

$$E_D = 4.229\ eV + 0.326469\ eV = 4.556\ eV \qquad (11.302)$$

The experimental bond energy of the deuterium molecule [22] is

$$E_D = 4.556\ eV \qquad (11.303)$$

VIBRATION OF THE HYDROGEN MOLECULE

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for H_2 given by Eq. (11.218) is

$$\omega(0)=\sqrt{\frac{k(0)}{\mu}}=\sqrt{\frac{621.98\ Nm^{-1}}{\mu}}=8.62385\ X\ 10^{14}\ radians/s \tag{11.304}$$

The spring constant, $k(0)$, for H_2 given by Eq. (11.219) is

$$k(0)=621.98\ Nm^{-1} \tag{11.305}$$

wherein $p=1$. The vibrational energy, $E_{vib}(0)$, of H_2 during bond formation given by Eq. (11.220) is

$$E_{vib}(0)=0.56764\ eV \tag{11.306}$$

The amplitude of oscillation given by Eq. (11.221) is

$$A(0)=\frac{\sqrt{\hbar}}{2^{3/2}\left(p^4 621.98\ Nm^{-1}\mu\right)^{1/4}}=4.275\ X\ 10^{-12}\ m=0.08079a_o \tag{11.307}$$

The vibrational energy for the H_2 $\upsilon=1\rightarrow\upsilon=0$ transition given by Eq. (11.223) is

$$E_{vib}(1)=0.517\ eV \tag{11.308}$$

The experimental vibrational energy of H_2 [25-26] is

$$E_{vib}(1)=0.5159\ eV \tag{11.309}$$

The anharmonicity term of H_2 given by Eq. (11.224) is

$$\omega_0 x_0=120.4\ cm^{-1} \tag{11.310}$$

The experimental anharmonicity term of H_2 from Huber and Herzberg [23] is

$$\omega_e x_e=121.33\ cm^{-1} \tag{11.311}$$

The vibrational energy for the D_2 $\upsilon=1\rightarrow\upsilon=0$ transition given by Eq. (11.229) is

$$E_{vib}=0.371\ eV \tag{11.312}$$

The experimental vibrational energy of D_2 [14, 19] is

$$E_{vib}=0.371\ eV \tag{11.313}$$

The anharmonicity term of D_2 given by Eq. (11.230) is

$$\omega_0 x_0=60.93\ cm^{-1} \tag{11.314}$$

The experimental anharmonicity term of D_2 from NIST [19] is

$$\omega_e x_e=61.82\ cm^{-1} \tag{11.315}$$

The results of the determination of the bond, vibrational, total, and ionization energies, and internuclear distances for hydrogen and deuterium molecules and molecular

ions are given in Table 11.1. The calculated results are based on first principles and given in closed form equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Despite the predictions of standard quantum mechanics that preclude the imaging of a molecule orbital, the full three-dimensional structure of the outer molecular orbital of N_2 has been recently tomographically reconstructed [27]. The charge-density surface observed is similar to that shown in Figure 5 for H_2 which is direct evidence that electrons are not point-particle probability waves that have no form until they are "collapsed to a point" by measurement. Rather they are physical, two-dimensional equipotential charge density surfaces.

Table 11.1. The calculated and experimental parameters of H_2, D_2, H_2^+ and D_2^+.

Parameter	Calculated	Experimental	Eqs.	Ref. for Exp.
H_2 Bond Energy	4.478 eV	4.478 eV	11.300	22
D_2 Bond Energy	4.556 eV	4.556 eV	11.302	22
H_2^+ Bond Energy	2.654 eV	2.651 eV	11.269	22
D_2^+ Bond Energy	2.696 eV	2.691 eV	11.271	23
H_2 Total Energy	31.677 eV	31.675 eV	11.296	22, 28, 18[a]
D_2 Total Energy	31.760 eV	31.760 eV	11.297	19, 23[b]
H_2 Ionization Energy	15.425 eV	15.426 eV	11.298	28
D_2 Ionization Energy	15.463 eV	15.466 eV	11.299	23
H_2^+ Ionization Energy	16.253 eV	16.250 eV	11.267	22, 18[c]
D_2^+ Ionization Energy	16.299 eV	16.294 eV	11.268	19, 23[d]
H_2^+ Magnetic Moment	$9.274\,X\,10^{-24}\,JT^{-}$ μ_B	$9.274\,X\,10^{-24}\,JT^{-1}$ μ_B	13.1-13.7	29
Absolute H_2 Gas-Phase NMR Shift	-28.0 ppm	-28.0 ppm	11.411	30-31
H_2 Internuclear Distance[e]	0.748 Å $\sqrt{2}a_o$	0.741 Å	11.287	32
D_2 Internuclear Distance[e]	0.748 Å $\sqrt{2}a_o$	0.741 Å	11.287	32
H_2^+ Internuclear Distance[f]	1.058 Å $2a_o$	1.06 Å	11.256	22
D_2^+ Internuclear Distance[e]	1.058 Å $2a_o$	1.0559 Å	11.256	23
H_2 Vibrational Energy	0.517 eV	0.516 eV	11.308	25, 26
D_2 Vibrational Energy	0.371 eV	0.371 eV	11.313	14, 19
H_2 $\omega_e x_e$	120.4 cm^{-1}	121.33 cm^{-1}	11.310	23
D_2 $\omega_e x_e$	60.93 cm^{-1}	61.82 cm^{-1}	11.314	19
H_2^+ Vibrational Energy	0.270 eV	0.271 eV	11.277	14, 19

D_2^+ Vibrational Energy	0.193 eV	0.196 eV	11.281	19
H_2 J=1 to J=0 Rotational Energy[e]	0.0148 eV	0.01509 eV	13.45	22
D_2 J=1 to J=0 Rotational Energy[e]	0.00741 eV	0.00755 eV	13.37-13.45	22
H_2^+ J=1 to J=0 Rotational Energy[f]	0.00740 eV	0.00739 eV	13.49	22
D_2^+ J=1 to J=0 Rotational Energy[e]	0.00370 eV	0.003723 eV	13.37-13.43, 13.49	23

[a] The experimental total energy of the hydrogen molecule is given by adding the first (15.42593 eV) [28] and second (16.2494 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the hydrogen atom (12.59844 eV) [18] and the bond energy of H_2^+ (2.651 eV) [22].

[b] The experimental total energy of the deuterium molecule is given by adding the first (15.466 eV) [23] and second (16.294 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the deuterium atom (12.603 eV) [19] and the bond energy of D_2^+ (2.692 eV) [23].

[c] The experimental second ionization energy of the hydrogen molecule, IP_2, is given by the sum of the ionization energy of the hydrogen atom (12.59844 eV) [18] and the bond energy of H_2^+ (2.651 eV) [22].

[d] The experimental second ionization energy of the deuterium molecule, IP_2, is given by the sum of the ionization energy of the deuterium atom (12.603 eV) [19] and the bond energy of D_2^+ (2.692 eV) [23].

[e] The internuclear distances are not corrected for the reduction due to $\overline{E}_{osc}$.

[f] The internuclear distances are not corrected for the increase due to $\overline{E}_{osc}$.

THE DIHYDRINO MOLECULAR ION $H_2[2c' = a_o]^+$

FORCE BALANCE OF THE DIHYDRINO MOLECULAR ION

Force balance between the electric and centrifugal forces of $H_2^+(1/2)$ is given by Eq. (11.115) where $p = 2$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2pe^2}{8\pi\varepsilon_o a b^2} D \tag{11.316}$$

which has the parametric solution given by Eq. (11.83) when

$$a = a_o \tag{11.317}$$

The semimajor axis, a, is also given by Eq. (11.116) where $p = 2$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.111) where $p = 2$.

$$2c' = a_o \tag{11.318}$$

The semiminor axis is given by Eq. (11.112) where $p = 2$.

$$b = \frac{\sqrt{3}}{2} a_o \tag{11.319}$$

The eccentricity, e, is given by Eq. (11.113).

$$e = \frac{1}{2} \tag{11.320}$$

ENERGIES OF THE DIHYDRINO MOLECULAR ION

The potential energy, V_e, of the electron MO in the field of magnitude twice that of the protons at the foci ($\xi = 0$) is given by Eq. (11.117) where $p = 2$

$$V_e = \frac{-8e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \tag{11.321}$$

The potential energy, V_p, due to proton-proton repulsion in the field of magnitude twice that of the protons at the foci ($\xi = 0$) is given by Eq. (11.120) where $p = 2$

$$V_p = \frac{2e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \tag{11.322}$$

The kinetic energy, T, of the electron MO is given by Eq. (11.119) where $p = 2$

$$T = \frac{2\hbar^2}{m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \tag{11.323}$$

Substitution of a and b given by Eqs. (11.317) and (11.319), respectively, into Eqs. (11.321-11.323) and using Eqs. (11.191-11.193) with $p = 2$ gives

$$V_e = \frac{-16e^2}{8\pi\varepsilon_o a_o} \ln 3 = -239.16\ eV \tag{11.324}$$

$$V_p = \frac{4e^2}{8\pi\varepsilon_o a_o} = 54.42\ eV \tag{11.325}$$

$$T = \frac{8e^2}{8\pi\varepsilon_o a_o} \ln 3 = 119.58\ eV \tag{11.326}$$

$$E_T = V_e + V_p + T + \bar{E}_{osc} \tag{11.327}$$

$$E_T = -2^2\left\{\frac{e^2}{8\pi\varepsilon_o a_H}(4\ln 3 - 1 - 2\ln 3)\left[1 + 2\sqrt{\frac{2\hbar\sqrt{\frac{2e^2}{4\pi\varepsilon_o (2a_H)^3}}}{m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$
$$= -2^2(16.13392\ eV) - 2^3(0.118755\ eV) \tag{11.328}$$
$$= -65.49\ eV$$

where Eqs. (11.324-11.326) are equivalent to Eqs. (11.122-11.124) with $p = 2$. The bond dissociation energy, E_D, given by Eq. (11.198) with $p = 2$ is the difference between the total energy of the corresponding hydrino atom and E_T given by Eq. (11.328):

$$E_D = E_T(H(1/p)) - E_T(H_2^+(1/p))$$
$$= 2^2(2.535\ eV) + 2^3(0.118755\ eV) \tag{11.329}$$
$$= 11.09\ eV$$

VIBRATION OF THE DIHYDRINO MOLECULAR ION

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for $H_2^+(1/2)$ from Eq. (11.160) is

$$\omega(0) = 2^2\sqrt{\frac{165.51\ Nm^{-1}}{\mu}} = 1.78\ X\ 10^{15}\ radians/s \tag{11.330}$$

wherein $p = 2$. The spring constant, $k(0)$, for $H_2^+(1/2)$ from Eq. (11.162) is

$$k(0) = 2^4 165.51\ Nm^{-1} = 2648\ Nm^{-1} \tag{11.331}$$

The amplitude of oscillation from Eq. (11.164) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(2^4(165.51)\ Nm^{-1}\mu\right)^{1/4}} = \frac{5.952\ X\ 10^{-12}\ m}{2} = \frac{0.1125 a_o}{2} \tag{11.332}$$

The vibrational energy, $E_{vib}(1)$, for the $\upsilon = 1 \rightarrow \upsilon = 0$ transition given by Eq. (11.166) is

$$E_{vib}(1) = 2^2(0.270\ eV) = 1.08\ eV \tag{11.333}$$

THE DIHYDRINO MOLECULE $H_2\left[2c'=\frac{a_o}{\sqrt{2}}\right]$

FORCE BALANCE OF THE DIHYDRINO MOLECULE

The force balance equation for the dihydrino molecule $H_2(1/2)$ is given by Eq. (11.200) where $p=2$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{2e^2}{8\pi\varepsilon_o a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{11.334}$$

which has the parametric solution given by Eq. (11.83) when

$$a = \frac{a_o}{2} \tag{11.335}$$

The semimajor axis, a, is also given by Eq. (11.202) where $p=2$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (11.204) where $p=2$.

$$2c' = \frac{1}{\sqrt{2}} a_o \tag{11.336}$$

The semiminor axis is given by Eq. (11.205) where $p=2$.

$$b = c = \frac{1}{2\sqrt{2}} a_o \tag{11.337}$$

The eccentricity, e, is given by Eq. (11.206).

$$e = \frac{1}{\sqrt{2}} \tag{11.338}$$

ENERGIES OF THE DIHYDRINO MOLECULE

The energies of the dihydrino molecule $H_2(1/2)$ are given by Eqs. (11.207-11.210) and Eqs. (11.239-11.241) with $p=2$

$$V_e = \frac{-4e^2}{8\pi\varepsilon_o \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -271.34\ eV \tag{11.339}$$

$$V_p = \frac{2}{8\pi\varepsilon_o} \frac{e^2}{\sqrt{a^2-b^2}} = 76.97\ eV \tag{11.340}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 135.67\ eV \tag{11.341}$$

The energy, V_m, of the magnetic force is

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -67.84\ eV \tag{11.342}$$

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc} \tag{11.343}$$

$$\begin{aligned} E_T &= -2^2 \left\{ \frac{e^2}{8\pi\varepsilon_o a_0} \left[\left(2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2} \right) \ln \frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2} \right] \left[1 + 2\sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o a_0^3}}}{m_e c^2}} \right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\} \\ &= -2^2 (31.351\ eV) - 2^3 (0.326469\ eV) \\ &= -128.02\ eV \end{aligned} \tag{11.344}$$

where Eqs. (11.339-11.342) are equivalent to Eqs. (11.207-11.210) with $p = 2$. The bond dissociation energy, E_D, given by Eq. (11.252) with $p = 2$ is the difference between the total energy of the corresponding hydrino atoms and E_T given by Eq. (11.344).

$$\begin{aligned} E_D &= E_T(2H(1/p)) - E_T(H_2(1/p)) \\ &= 2^2 (4.151\ eV) + 2^3 (0.326469\ eV) \\ &= 19.22\ eV \end{aligned} \tag{11.345}$$

VIBRATION OF THE DIHYDRINO MOLECULE

It can be shown that a perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit [11]. The resonant vibrational frequency for the $H_2(1/2)$ from Eq. (11.217) is

$$\omega(0) = 2^2\sqrt{\frac{k}{\mu}} = 2^2\sqrt{\frac{621.98\ Nm^{-1}}{\mu}} 3.45\ X\ 10^{15}\ radians/s \tag{11.346}$$

wherein $p = 2$. The spring constant, $k(0)$, for $H_2(1/2)$ from Eq. (11.219) is

$$k(0) = 2^4 621.98\ Nm^{-1} = 9952\ Nm^{-1} \tag{11.347}$$

The amplitude of oscillation from Eq. (11.221) is

$$A(0) = \frac{\sqrt{\hbar}}{2^{3/2}\left(2^4 (621.98)\ Nm^{-1}\mu\right)^{1/4}} = \frac{4.275\ X\ 10^{-12}\ m}{2} = \frac{0.08079 a_o}{2} \tag{11.348}$$

The vibrational energy, $E_{vib}(1)$, of $H_2(1/2)$ from Eq. (11.223) is

$$E_{vib}(1) = 2^2 (0.517)\ eV = 2.07\ eV \tag{11.349}$$

GEOMETRY

The internuclear distance can also be determined geometrically. The spheroidal MO of the hydrogen molecule is an equipotential energy surface, which is an energy minimum surface. For the hydrogen molecule, the electric field is zero for $\xi > 0$. Consider two hydrogen atoms A and B approaching each other. Consider that the two electrons form a spheroidal MO as the two atoms overlap, and the charge is distributed such that an equipotential two-dimensional surface is formed. The electric fields of atoms A and B add vectorially as the atoms overlap. The energy at the point of intersection of the overlapping orbitspheres decreases to a minimum as they superimpose and then rises with further overlap. When this energy is a minimum the internuclear distance is determined. It can be demonstrated [33] that when two hydrogen orbitspheres superimpose such that the radial electric field vector from nucleus A and B makes a 45° angle with the point of intersection of the two original orbitspheres, the electric energy of interaction between orbitspheres given by

$$E_{\text{interaction}} = 2\,X\,\frac{1}{2}\varepsilon_o \int \Delta \mathbf{E}^2 dv \tag{11.350}$$

is a minimum (Figure 7.1 of [33]). The MO is a minimum potential energy surface; therefore, a minimum of energy of one point on the surface is a minimum for the entire surface of the MO. Thus,

$$R_{H_2} = \sqrt{2}a_o = 0.748\text{Å} \tag{11.351}$$

The experimental internuclear bond distance is $0.746\,\text{Å}$.

DIHYDRINO IONIZATION ENERGIES

The first ionization energy, IP_1, of the dihydrino molecule

$$H_2(1/p) \rightarrow H_2^+(1/p) + e^- \tag{11.352}$$

is given by Eq. (11.244) with $p = 2$.

$$IP_1 = E_T\left(H_2^+(1/p)\right) - E_T\left(H_2(1/p)\right) \tag{11.353}$$

$$IP_1 = 2^2(15.2171\ eV) + 2^3(0.2077\ eV) = 62.53\ eV \tag{11.354}$$

The second ionization energy, IP_2, is given by Eq. (11.245) with $p = 2$.

$$IP_2 = 2^2(16.13392\ eV) + 2^3(0.118755\ eV) = 65.49\ eV \tag{11.355}$$

A hydrino atom can react with a hydrogen, deuterium, or tritium nucleus to form a dihydrino molecular ion that further reacts with an electron to form a dihydrino molecule.

$$H(1/p)+H^{+}+e- \rightarrow H_2(1/p) \tag{11.356}$$

The energy released is

$$E = E(H(1/p)) - E_T \tag{11.357}$$

where E_T is given by Eq. (11.241).

A hydrino atom can react with a hydrogen, deuterium, or tritium atom to form a dihydrino molecule.

$$H(1/p)+H \rightarrow H_2(1/p) \tag{11.358}$$

The energy released is

$$E = E\left(H(1/p)\right)+E(H)-E_T \tag{11.359}$$

where E_T is given by Eq. (11.241).

SIZES OF REPRESENTATIVE ATOMS AND MOLECULES

ATOMS

Helium Atom (He)

Helium comprises the nucleus at the origin and two electrons as a spherical shell at $r = 0.567a_0$.

Hydrogen Atom ($\mathbf{H}[\mathbf{a_H}]$)

Hydrogen comprises the nucleus at the origin and the electron as a spherical shell at $r = a_H$.

Hydrino Atom ($\mathbf{H}\left[\frac{\mathbf{a_H}}{\mathbf{2}}\right]$)

Hydrino atom (1/2) comprises the nucleus at the origin and the electron as a spherical shell at $r = \frac{a_H}{2}$.

MOLECULES

Hydrogen Molecular Ion ($\mathbf{H_2}[\mathbf{2c' = 2a_0}]^{+}$)

$a = 2a_0$

$$b = c = \sqrt{3}a_0$$

$$c' = a_0$$

$$2c' = 2a_0$$

Hydrogen Molecule ($\mathbf{H_2}\left[\mathbf{2c' = \sqrt{2}a_0}\right]$)

$$a = a_0$$

$$b = c = \frac{1}{\sqrt{2}}a_0$$

$$c' = \frac{1}{\sqrt{2}}a_0$$

$$2c' = \sqrt{2}a_0$$

Dihydrino Molecular Ion ($\mathbf{H_2}\left[\mathbf{2c' = a_0}\right]^+$)

$$a = a_0$$

$$b = c = \frac{\sqrt{3}}{2}a_0$$

$$b = c = \frac{1}{2}a_0$$

$$2c' = a_0$$

Dihydrino Molecule ($\mathbf{H_2}\left[\mathbf{2c' = \frac{1}{\sqrt{2}}a_0}\right]$)

$$a = \frac{1}{2}a_0$$

$$b = c = \frac{1}{2\sqrt{2}}a_0$$

$$c' = \frac{1}{2\sqrt{2}}a_0$$

$$2c' = \frac{1}{\sqrt{2}}a_0$$

ORTHO-PARA TRANSITION OF HYDROGEN-TYPE MOLECULES

Each proton of hydrogen-type molecules possesses a magnetic moment, which is derived in the Proton and Neutron section and is given by

$$\mu_P = \frac{\left(\frac{2}{3}\right)^2 e\hbar}{2\frac{m_p}{2\pi}} \tag{11.360}$$

The magnetic moment, $\mathbf{m}$, of the proton is given by Eq. (11.360), and the magnetic field of the proton follows from the relationship between the magnetic dipole field and the magnetic moment, $\mathbf{m}$, as given by Jackson [34] where $\mathbf{m} = \mu_P \mathbf{i}_z$.

$$\mathbf{H} = \frac{\mu_P}{r^3}(\mathbf{i}_r 2\cos\theta - \mathbf{i}_\theta \sin\theta) \tag{11.361}$$

Multiplication of Eq. (11.361) by the permeability of free space, μ_0, gives the magnetic flux, $\mathbf{B}$, due to proton one at proton two.

$$\mathbf{B} = \frac{\mu_0 \mu_P}{r^3}(\mathbf{i}_r 2\cos\theta - \mathbf{i}_\theta \sin\theta) \tag{11.362}$$

$\Delta E_{mag}^{\text{ortho/para}}$, the energy to flip the orientation of proton two's magnetic moments, μ_P, from ortho (parallel magnetic moments) to para (antiparallel magnetic moments) with respect to the direction of the magnetic moment of proton one with corresponding magnetic flux $\mathbf{B}$ is

$$\Delta E_{mag}^{\text{ortho/para}} = -2\mu_P \mathbf{B} = \frac{-2\mu_0 {\mu_P}^2}{r^3} \tag{11.363}$$

where r is the internuclear distance 2c' where c' is given by Eq. (11.204). Substitution of the internuclear distance into Eq. (11.363) for r gives

$$\Delta E_{mag}^{\text{ortho/para}} = -2\mu_P \mathbf{B} = \frac{-2\mu_0 {\mu_P}^2 p^3}{\left(\sqrt{2}a_o\right)^3} \tag{11.364}$$

The frequency, f, can be determined from the energy using the Planck relationship, Eq. (2.18).

$$f = \frac{\Delta E_{mag}^{\text{ortho/para}}}{h} = \frac{\frac{-2\mu_0 {\mu_P}^2 p^3}{\left(\sqrt{2}a_o\right)^3}}{h} \tag{11.365}$$

From Eq. (11.365) with $p = 2$, the ortho-para transition energy of the dihydrino molecule is 14.4 *MHz*.

NUCLEAR MAGNETIC RESONANCE SHIFT

The proton gyromagnetic ratio, $\gamma_p / 2\pi$, is

$$\gamma_P / 2\pi = 42.57602\ MHz\ T^{-1} \tag{11.366}$$

The NMR frequency, f, is the product of the proton gyromagnetic ratio given by Eq. (11.366) and the magnetic flux, $\mathbf{B}$.

$$f = \gamma_P / 2\pi \mathbf{B} = 42.57602\ MHz\ T^{-1}\mathbf{B} \tag{11.367}$$

A typical flux for a superconducting NMR magnet is $1.5\ T$. According to Eq. (11.367) this corresponds to a radio frequency (RF) of $63.86403\ MHz$. With a constant magnetic field, the frequency is scanned to yield the spectrum where the frequency scan is typically achieved using a Fourier transform on the free induction decay signal following a radio frequency pulse. Or, in a less common type of NMR spectrometer, the radiofrequency is held constant (e.g. $60\ MHz$), the applied magnetic field, H_0 ($H_0 = \frac{B}{\mu_0}$), is varied over a small range, and the frequency of energy absorption is recorded at the various values for H_0. The spectrum is typically scanned and displayed as a function of increasing H_0. The protons that absorb energy at a lower H_0 give rise to a downfield absorption peak; whereas, the protons that absorb energy at a higher H_0 give rise to an upfield absorption peak. The electrons of the compound of a sample influence the field at the nucleus such that it deviates slightly from the applied value. For the case that the chemical environment has no NMR effect, the value of H_0 at resonance with the radiofrequency held constant at $60\ MHz$ is

$$\frac{2\pi f}{\mu_0 \gamma_P} = \frac{(2\pi)(60\ MHz)}{\mu_0 42.57602\ MHz\ T^{-1}} = H_0 \tag{11.368}$$

In the case that the chemical environment has a NMR effect, a different value of H_0 is required for resonance. This chemical shift is proportional to the electronic magnetic flux charge at the nucleus due to the applied field, which in the case of each dihydrino molecule is a function of its semimajor and semiminor axes as shown *infra*.

Consider the application of a z-axis-directed uniform external magnetic flux, $\mathbf{B}_z$, to a dihydrino molecule comprising prolate spheroidal electron MOs with two spin-paired electrons. The diamagnetic reaction current increases or decreases the MO current to counteract any applied flux according to Lenz's law as shown in the Hydrino Hydride Ion Nuclear Magnetic Resonance Shift section. The current of hydrogen-type molecules is along

elliptical orbits parallel to the semimajor axis. Thus, the electronic interaction with the nuclei requires that each nuclear magnetic moment is in the direction of the semiminor axis. Thus, the nuclei are NMR active towards $\mathbf{B}_z$ when the orientation of the semimajor axis, a, is along the x-axis, and the semiminor axes, $b = c$, are along the y-axis and z-axis, respectively. The flux is applied over the time interval $\Delta t = t_i - t_f$ such that the field increases at a rate dB/dt. The electric field, $\mathbf{E}$, along a perpendicular elliptic path of the dihydrino MO at the plane $z = 0$ is given by

$$\oint E \cdot ds = \int \frac{dB}{dt} \cdot dA \tag{11.369}$$

The induced electric field must be constant along the path; otherwise, compensating currents would flow until the electric field is constant. Thus, Eq. (11.369) becomes

$$E = \frac{\int \frac{dB}{dt} \cdot dA}{\oint ds} = \frac{\int \frac{dB}{dt} \cdot dA}{4aE(k)} = \frac{\pi ab \frac{dB}{dt}}{4aE(k)} \tag{11.370}$$

where $E(k)$ is the elliptic integral given by

$$E(k) = \int_0^{\frac{\pi}{2}} \sqrt{1 - k \sin^2 \phi} d\phi = 1.2375 \tag{11.371}$$

$$k = e = \frac{\sqrt{a^2 - b^2}}{a} = \frac{\sqrt{2}}{2} \tag{11.372}$$

the area of an ellipse, A, is

$$A = \pi ab \tag{11.373}$$

the perimeter of an ellipse, s, is

$$s = 4aE(k) \tag{11.374}$$

a is the semimajor axis given by Eq. (11.202), b is the semiminor axis given by Eq. (11.205), and e is the eccentricity given by Eq. (11.206). The acceleration along the path, dv/dt, during the application of the flux is determined by the electric force on the charge density of the electrons:

$$m_e \frac{dv}{dt} = eE = \frac{e\pi ab}{4aE(k)} \frac{dB}{dt} \tag{11.375}$$

Thus, the relationship between the change in velocity, v, and the change in B is

$$dv = \frac{e\pi ab}{4aE(k) m_e} dB \tag{11.376}$$

Let Δv represent the net change in v over the time interval $\Delta t = t_i - t_f$ of the application of the flux. Then,

$$\Delta v = \int_{v_0}^{v_0+\Delta v} dv = \frac{e\pi ab}{4aE(k)m_e}\int_0^B dB = \frac{e\pi abB}{4aE(k)m_e} \tag{11.377}$$

The average current, I, of a charge moving time harmonically along an ellipse is

$$I = ef = \frac{ev}{4aE(k)} \tag{11.378}$$

where f is the frequency. The corresponding magnetic moment is given by

$$m = AI = \pi abI = \frac{\pi abev}{4aE(k)} \tag{11.379}$$

Thus, from Eqs. (11.377) and (11.379), the change in the magnetic moment, $\Delta\mathbf{m}$, due to an applied magnetic flux, $\mathbf{B}$, is [35]

$$\Delta\mathbf{m} = -\frac{(e\pi ab)^2\mathbf{B}}{(4aE(k))^2 m_e} \tag{11.380}$$

Next, the contribution from all plane cross sections of the prolate spheroid MO must be integrated along the z-axis. The spheroidal surface is given by

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{b^2}=1 \tag{11.381}$$

The intersection of the plane $z = z'$ $(-b \le z' \le b)$ with the spheroid determines the curve

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}=1-\frac{z'^2}{b^2} \tag{11.382}$$

or

$$\frac{x^2}{a^2\left(1-\frac{z'^2}{b^2}\right)}+\frac{y^2}{b^2\left(1-\frac{z'^2}{b^2}\right)}=1 \tag{11.383}$$

Eq. (11.383) is an ellipse with semimajor axis, a', and semiminor axis, b', given by

$$a' = a\sqrt{1-\frac{z'^2}{b^2}} \tag{11.384}$$

$$b' = b\sqrt{1-\frac{z'^2}{b^2}} \tag{11.385}$$

The eccentricity, e', is given by

$$e' = \frac{\sqrt{a^2\left(1-\frac{z'^2}{b^2}\right)-b^2\left(1-\frac{z'^2}{b^2}\right)}}{a\sqrt{1-\frac{z'^2}{b^2}}} = \frac{\sqrt{a^2-b^2}}{a} = e \tag{11.386}$$

where e is given by Eq. (11.372). The area, A', is given by

$$A' = \pi a' b' \tag{11.387}$$

and the perimeter, s', is given by

$$s' = 4a'E(k) = 4aE(k)\sqrt{1-\frac{z'^2}{b^2}} = s\sqrt{1-\frac{z'^2}{b^2}} \tag{11.388}$$

where s is given by Eq. (11.374). The differential magnetic moment change along the z-axis is

$$d\Delta\mathbf{m} = -\frac{1}{2b}\frac{\left(e\pi a' b'\right)^2 \mathbf{B}}{\left(4a'E(k)\right)^2 m_e} dz' \tag{11.389}$$

Using Eq. (11.385) for the parameter b', the change in magnetic moment for the dihydrino molecule is given by the integral over $-b \le b' \le b$:

$$\Delta\mathbf{m} = -\frac{1}{2b}\int_{-b}^{b}\frac{\left(e\pi a' b\sqrt{1-\frac{z'^2}{b^2}}\right)^2 \mathbf{B}}{\left(4a'E(k)\right)^2 m_e} dz' = -C_1\frac{1}{m_e}\left(\frac{\pi e}{4E(k)}\right)^2 \tag{11.390}$$

Then, integral to correct for the z-dependence of b' is

$$C_1 = \frac{\int_{-b}^{b}\left(b^2-z^2\right)dz}{2b} = \frac{2}{3}b^2 = \frac{a_0^2}{3p} \tag{11.391}$$

where the semiminor axis, $b = \frac{a_0}{p\sqrt{2}}$, given by Eq. (11.205) was used.

The change in magnetic moment would be given by the substitution of Eq. (11.391) into Eq. (11.390), if the change density were constant along the path of Eqs. (11.370) and (11.378), but it is not. The charge density of the MO in rectangular coordinates (Eq. (11.42)) is

$$\sigma = \frac{e}{4\pi abc}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{11.392}$$

(The mass-density function of an MO is equivalent to its charge-density function where m replaces q of Eq. (11.42)). The equation of the plane tangent to the ellipsoid at the point x_0, y_0, z_0 is

$$X\frac{x_0}{a^2}+Y\frac{y_0}{b^2}+Z\frac{z_0}{c^2}=1 \tag{11.393}$$

where X, Y, Z are running coordinates in the plane. After dividing through by the square root of the sum of the squares of the coefficients of X, Y, and Z, the right member is the distance D from the origin to the tangent plane. That is,

$$D=\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{11.394}$$

so that

$$\sigma=\frac{e}{4\pi abc}D \tag{11.395}$$

In other words, the surface density at any point on the ellipsoidal MO is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin. In order to maintain current continuity, the diamagnetic velocity of Eq. (11.377) must be a constant along any given path integral corresponding to a constant electric field. Consequently, the charge density must be the minimum value of that given by Eq. (11.392). The minimum corresponds to $y=b$ and $x=z=0$ such that the charge density is

$$\sigma=\frac{e}{4\pi ab^2}\frac{1}{\sqrt{\frac{0^2}{a^4}+\frac{b^2}{b^4}+\frac{0^2}{b^4}}}=\frac{e}{4\pi ab} \tag{11.396}$$

The MO is an equipotential surface, and the current must be continuous over the two-dimensional surface. Continuity of the surface current density, K, due to the diamagnetic effect of the applied magnetic field on the MO and the equipotential boundary condition require that the current of each elliptical curve determined by the intersection of the plane $z=z'$ $(-b\le z'\le b)$ with the spheroid be the same. The charge density is spheroidally symmetrical about the semimajor axis. Thus, λ, the charge density per unit length along each elliptical path cross section of Eq. (11.383) is given by distributing the surface charge density of Eq. (11.396) uniformly along the z-axis for $-b\le z'\le b$. So, $\lambda(z'=0)$, the linear charge density λ in the plane $z'=0$, is

$$\lambda(z'=0)=\frac{\sigma}{\frac{1}{2b}}=\frac{e}{4\pi ab}2b=\frac{e}{2\pi a} \tag{11.397}$$

And, the linear charge density must be equally distributed over each elliptical path cross section corresponding to each plane $z=z'$. The current is independent of z' when the linear charge density, $\lambda(z')$, is normalized for the path length:

$$\lambda(z')=\frac{e}{2\pi a}\frac{4aE(k)}{4a'E(k')}=\frac{e}{2\pi a'} \tag{11.398}$$

where the equality of the eccentricities of each elliptical plane cross section given by Eq. (11.386) was used. Substitution of Eq. (11.388) for the corresponding charge density, $\frac{e}{4a'E(k)}$, of Eq. (11.390) and using Eq. (11.391) gives

$$\Delta\mathbf{m}=\frac{2}{3}\frac{e^2b^2\mathbf{B}}{4m_e}=\frac{e^2a_0^2\mathbf{B}}{12p^2m_e} \tag{11.399}$$

The two electrons are spin-paired and the velocities are mirror opposites. Thus, the change in velocity of each electron treated individually (Eq. (10.3)) due to the applied field would be equal and opposite. However, as shown in the Three Electron Atom section, the two paired electrons may be treated as one with twice the mass where m_e is replaced by $2m_e$ in Eq. (11.399). In this case, the paired electrons spin together about the applied field axis, the z-axis, to cause a reduction in the applied field according to Lenz's law. Thus, from Eq. (11.399), the change in magnetic moment is given by

$$\Delta\mathbf{m}=\frac{e^2a_0^2\mathbf{B}}{24p^2m_e} \tag{11.400}$$

The opposing diamagnetic flux is uniform, parallel, and opposite the applied field as given by Stratton [36]. Specifically, the change in magnetic flux, $\Delta\mathbf{B}$, at the nucleus due to the change in magnetic moment, $\Delta\mathbf{m}$, is

$$\Delta\mathbf{B}=\mu_0A_2\Delta\mathbf{m} \tag{11.401}$$

where μ_0 is the permeability of vacuum,

$$A_2=\int_0^\infty\frac{ds}{(s+b^2)R_s} \tag{11.402}$$

is an elliptic integral of the second kind given by Whittaker and Watson [37], and

$$R_s=(s+b^2)\sqrt{(s+a^2)} \tag{11.403}$$

Substitution of Eq. (11.403) into Eq. (11.402) gives

$$A_2 = \int_0^\infty \frac{ds}{\left(s+b^2\right)^2\left(s+a^2\right)^{1/2}} \tag{11.404}$$

From integral 154 of Lide [38]:

$$A_2 = -\left\{\frac{1}{a^2-b^2}\frac{\sqrt{s+a^2}}{s+b^2}\right\}_0^\infty - \frac{1}{2}\frac{1}{a^2-b^2}\int_0^\infty \frac{ds}{\left(s+b^2\right)\sqrt{s+a^2}} \tag{11.405}$$

The evaluation at the limits of the first integral is

$$-\left\{\frac{1}{a^2-b^2}\frac{\sqrt{s+a^2}}{s+b^2}\right\}_0^\infty = \frac{a}{b^2\left(a^2-b^2\right)} \tag{11.406}$$

From integral #147 of Lide [9], the second integral is:

$$-\frac{1}{2}\frac{1}{a^2-b^2}\int_0^\infty \frac{ds}{\left(s+b^2\right)\sqrt{s+a^2}} = \left\{\frac{1}{2}\frac{1}{\left(a^2-b^2\right)^{3/2}}\ln\frac{\sqrt{s+a^2}+\sqrt{a^2-b^2}}{\sqrt{s+a^2}-\sqrt{a^2-b^2}}\right\}_0^\infty \tag{11.407}$$

Evaluation at the limits of the second integral gives

$$-\frac{1}{2}\frac{1}{\left(a^2-b^2\right)^{3/2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{11.408}$$

Combining Eq. (11.406) and Eq. (11.408) gives

$$A_2 = \frac{a}{b^2\left(a^2-b^2\right)} - \frac{1}{2}\frac{1}{\left(a^2-b^2\right)^{3/2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \frac{p^3 4}{a_0^3} - \frac{p^3\sqrt{2}}{a_0^3}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} \tag{11.409}$$

where the semimajor axis, $a = \frac{a_0}{p}$, given by Eq. (11.202) and the semiminor axis, $b = \frac{a_0}{p\sqrt{2}}$, given by Eq. (11.205) were used.

Substitution of Eq. (11.400) and Eq. (11.409) into Eq. (11.401) gives

$$\Delta\mathbf{B} = -\mu_0\left(\frac{p^3 4}{a_0^3} - \frac{p^3\sqrt{2}}{a_0^3}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{a_0^2 e^2\mathbf{B}}{24p^2 m_e} \tag{11.410}$$

Additionally, it is found both theoretically and experimentally that the dimensions, r^2, of the molecule corresponding to the area in Eqs. (11.369) and (11.379) used to derived Eq. (11.410) must be replaced by an average, $\langle r^2\rangle$, that takes into account averaging over the orbits isotropically oriented. The correction of 2/3 is given by Purcell [35]. In the case of hydrogen-type molecules, the electronic interaction with the nuclei require that each nuclear magnetic moment is in the direction of the semiminor axis. But free rotation about each of

three axes results in an isotropic averaging of 2/3 where the rotational frequencies of hydrogen-type molecules are much greater than the corresponding NMR frequency (e.g. 10^{12} *Hz* versus 10^{8} *Hz*). Thus, Eq. (11.410) gives the absolute upfield chemical shift, $\frac{\Delta B}{B}$, of H_2 relative to a bare proton:

$$\begin{aligned}\frac{\Delta \mathbf{B}}{\mathbf{B}} = \frac{\Delta B}{B} &= -\mu_0\left(\frac{p^3 4}{a_0^3} - \frac{p^3\sqrt{2}}{a_0^3}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{a_0^2 e^2}{36p^2 m_e} \\ &= -\mu_0\left(4-\sqrt{2}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{pe^2}{36a_0 m_e} \\ &= -p28.01\,ppm\end{aligned} \tag{11.411}$$

where $p=1$ for H_2.

It follows from Eqs. (11.202) and (11.411) that the diamagnetic flux (flux opposite to the applied field) at each nucleus is inversely proportional to the semimajor radius, $a=\frac{a_o}{p}$. For resonance to occur, ΔH_0, the change in applied field from that given by Eq. (11.368), must compensate by an equal and opposite amount as the field due to the electrons of the dihydrino molecule. According to Eq. (11.202), the ratio of the semimajor axis of the dihydrino molecule $H_2(1/p)$ to that of the hydrogen molecule H_2 is the reciprocal of an integer p. Similarly it is shown in the Hydrino Hydride Ion Nuclear Magnetic Resonance Shift section and previously [39], that according to Eq. (7.87) the ratio of the radius of the hydrino hydride ion $H^-(1/p)$ to that of the hydride ion $H^-(1/1)$ is the reciprocal of an integer p. It follows from Eqs. (7.90-7.96) that compared to a proton with no chemical shift, the ratio of ΔH_0 for resonance of the proton of the hydrino hydride ion $H^-(1/p)$ to that of the hydride ion $H^-(1/1)$ is a positive integer. That is, if only the radius is considered, the absorption peak of the hydrino hydride ion occurs at a value of ΔH_0 that is a multiple of p times the value that is resonant for the hydride ion compared to that of a proton with no shift. However, a hydrino hydride ion is equivalent to the ordinary hydride ion except that it is in a lower energy state. The source current of the state must be considered in addition to the reduced radius.

As shown in the Stability of "Ground" and Hydrino States section, for the below "ground" (fractional quantum number) energy states of the hydrogen atom, σ_{photon}, the two-

dimensional surface charge due to the "trapped photon" at the electron orbitsphere and phase-locked with the electron orbitsphere current, is given by Eqs. (5.08) and (2.11).

$$\sigma_{photon} = \frac{e}{4\pi(r_n)^2}\left[Y_0^0(\theta,\phi) - \frac{1}{n}\left[Y_0^0(\theta,\phi) + \mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\}\right]\right]\delta(r-r_n)$$

$$n = \frac{1}{p} = 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \ldots, \qquad (11.412)$$

And, $\sigma_{electron}$, the two-dimensional surface charge of the electron orbitsphere is

$$\sigma_{electron} = \frac{-e}{4\pi(r_n)^2}\left[Y_0^0(\theta,\phi) + \mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\}\right]\delta(r-r_n) \qquad (11.413)$$

The superposition of σ_{photon} (Eq. (11.412)) and $\sigma_{electron}$, (Eq. (11.413)) where the spherical harmonic functions satisfy the conditions given in the Angular Function section is

$$\sigma_{photon} + \sigma_{electron} = \frac{-e}{4\pi(r_n)^2}\left[\frac{1}{n}Y_0^0(\theta,\phi) + \left(1+\frac{1}{n}\right)\mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\}\right]\delta(r-r_n)$$

$$n = \frac{1}{p} = 1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \ldots, \qquad (11.414)$$

The ratio of the total charge distributed over the surface at the radius of the hydrino hydride ion $H^-(1/p)$ to that of the hydride ion $H^-(1/1)$ is an integer p, and the corresponding total source current of the hydrino hydride ion is equivalent to an integer p times that of an electron. The "trapped photon" obeys the phase-matching condition given in Excited States of the One-Electron Atom (Quantization) section, but does not interact with the applied flux directly. Only each electron does; thus, Δv of Eq. (11.377) must be corrected by a factor of $1/p$ corresponding to the normalization of the electron source current according to the invariance of charge under Gauss' Integral Law. As also shown by Eqs. (7.17-7.23) and (7.87), the "trapped photon" gives rise to a correction to the change in magnetic moment due to the interaction of each electron with the applied flux. The correction factor of $1/p$ consequently cancels the NMR effect of the reduced radius which is consistent with general observations on diamagnetism [40]. It follows that the same result applies in the case of Eq. (11.411) for $H_2(1/p)$ wherein the coordinates are ellipsoidal rather than spherical.

The cancellation of the chemical shift due to the reduced radius or the reduced semiminor and semimajor axes in the case of $H^-(1/p)$ and $H_2(1/p)$, respectively, by the corresponding source current is exact except for an additional relativistic effect. The relativistic effect for $H^-(1/p)$ arises due to the interaction of the currents corresponding to

the angular momenta of the "trapped photon" and the electrons and is analogous to that of the fine structure of the hydrogen atom involving the ${}^2P_{3/2}$—${}^2P_{1/2}$ transition. The derivation follows that of the fine structure given in the Spin-Orbital Coupling section.

$\frac{e}{m_e}$ of the electron, the electron angular momentum of $\hbar$, and the electron magnetic momentum of μ_B are invariant for any electronic state. The same applies for the paired electrons of hydrino hydride ions. The condition that flux must be linked by the electron in units of the magnetic flux quantum in order to conserve the invariant electron angular momentum of $\hbar$ gives the additional chemical shift due to relativistic effects. Using Eqs. (2.159-2.160), Eq. (2.166) may be written as

$$E_{s/o} = \frac{\alpha\pi\mu_0 e^2\hbar^2}{m_e^2 r^3}\sqrt{\frac{3}{4}} = \alpha 2\pi 2\frac{e\hbar}{2m_e}\frac{\mu_0 e\hbar}{2m_e a_0^3}\sqrt{\frac{3}{4}} = \alpha 2\pi 2\mu_B B \tag{11.415}$$

From Eq. (11.415) and Eq. (1.205), the relativistic stored magnetic energy contributes a factor of $\alpha 2\pi$ In spherical coordinates, the relativistic change in flux $\Delta\mathbf{B}_{SR}$ may be calculated using Eq. (7.95) and the relativistic factor of $\gamma_{SR} = 2\pi\alpha$ which is the same as that given by Eq. (1.229):

$$\Delta\mathbf{B}_{SR} = -\gamma_{SR}\mu_0\frac{\Delta m}{r_n^3}(\mathbf{i}_r\cos\theta - \mathbf{i}_\theta\sin\theta) = -2\pi\alpha\mu_0\frac{\Delta m}{r_n^3}(\mathbf{i}_r\cos\theta - \mathbf{i}_\theta\sin\theta) \tag{11.416}$$

for $r < r_n$.

The stored magnetic energy term of the electron g factor of each electron of a dihydrino molecule is the same as that of a hydrogen atom since $\frac{e}{m_e}$ is invariant and the invariant angular momentum and magnetic moment of the former are also $\hbar$ and μ_B, respectively, as given in the Magnetic Moment of an Ellipsoidal MO and Magnetic Field of an Ellipsoidal MO sections. Thus, the corresponding correction in ellipsoidal coordinates follows from Eq. (2.166) wherein the result of the length contraction for the circular path in spherical coordinates is replaced by that of the elliptical path.

The only position on the elliptical path at which the current is perpendicular to the radial vector defined by the central force of the protons is at the semimajor axis. It was shown in the Special Relativistic Correction to the Ionization Energies section that when the condition that the electron's motion is tangential to the radius is met, the radius is Lorentzian invariant. That is, for the case that k is the lightlike k^0, with $k = \omega_n / c$, a is invariant. In

the case of a spherically symmetrical MO such as the case of the hydrogen atom, it was also shown that this condition determines that the electron's angular momentum of $\hbar$, $\frac{e}{m_e}$ of Eq. (1.110), and the electron's magnetic moment of a Bohr magneton, μ_B, are invariant. The effect of the relativistic length contraction and time dilation for constant spherical motion is a change in the angle of motion with a corresponding decrease in the electron wavelength. The angular motion becomes projected onto the radial axis which contracts, and the extent of the decrease in the electron wavelength and radius due to the electron motion in the laboratory inertial frame are given by

$$\lambda = 2\pi r' \sqrt{1-\left(\frac{v}{c}\right)^2}\sin\left[\frac{\pi}{2}\left(1-\left(\frac{v}{c}\right)^2\right)^{3/2}\right]+r'\cos\left[\frac{\pi}{2}\left(1-\left(\frac{v}{c}\right)^2\right)^{3/2}\right] \tag{11.417}$$

and

$$r = r'\left[\sqrt{1-\left(\frac{v}{c}\right)^2}\sin\left[\frac{\pi}{2}\left(1-\left(\frac{v}{c}\right)^2\right)^{3/2}\right]+\frac{1}{2\pi}\cos\left[\frac{\pi}{2}\left(1-\left(\frac{v}{c}\right)^2\right)^{3/2}\right]\right] \tag{11.418}$$

respectively. Then, the relativistic factor γ^* is

$$\gamma^* = \frac{2\pi}{2\pi\sqrt{1-\left(\frac{v}{c}\right)^2}\sin\left[\frac{\pi}{2}\left(1-\left(\frac{v}{c}\right)^2\right)^{3/2}\right]+\cos\left[\frac{\pi}{2}\left(1-\left(\frac{v}{c}\right)^2\right)^{3/2}\right]} \tag{11.419}$$

where the velocity is given by Eq. (1.56) with the radius given by Eq. (1.233).

Each point or coordinate position on the continuous two-dimensional electron MO of the dihydrino molecule defines an infinitesimal mass-density element which moves along an elliptical orbit of a spheroidal MO in such a way that its eccentric angle, θ, changes at a constant rate. That is $\theta = \omega t$ at time t where ω is a constant, and

$$r(t) = \mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t \tag{11.420}$$

is the parametric equation of the ellipse. Next, special relativistic effects on distance and time are considered. The parametric radius, $r(t)$, is a minimum at the position of the semiminor axis of length b, and the motion is transverse to the radial vector. Since the angular momentum of $\hbar$ is constant, the electron wavelength without relativistic correction is given by

$$2\pi b = \lambda = \frac{h}{mv} \tag{11.421}$$

such that the angular momentum, L, is given by

$$L = r \times mv = bmv = \hbar \tag{11.422}$$

The nonradiation and the $\hbar$, $\frac{e}{m_e}$, and μ_B invariance conditions require that the angular frequencies, ω_s and ω_e, for spherical and ellipsoidal motion, respectively, are

$$\omega_s = \frac{\hbar}{m_e r^2} = \frac{\frac{\pi L}{m_e}}{A} \tag{11.423}$$

and

$$\omega_e = \frac{\pi\hbar}{m_e A} = \frac{\hbar}{m_e ab} \tag{11.424}$$

where A is the area of the closed orbit, the area of an ellipse given by Eq. (11.373). Since the angular frequency ω_e has the form as ω_s, the time dilation corrections are equivalent, where the correction for ω_s is given in the Special Relativistic Correction to the Ionization Energies section. Since the semimajor axis, a, is invariant, but b undergoes length contraction, the relationship between the velocity and the electron wavelength at the semiminor axis from Eq. (11.417) and Eq. (11.421) is

$$\lambda = 2\pi b\sqrt{1-\left(\frac{v}{c}\right)^2}\sin\left[\frac{\pi}{2}\left(1-\left(\frac{v}{c}\right)^2\right)^{3/2}\right] + a\cos\left[\frac{\pi}{2}\left(1-\left(\frac{v}{c}\right)^2\right)^{3/2}\right] \tag{11.425}$$

where $\lambda \to a$ as $v \to c$ replaces the spherical coordinate result of $\lambda \to r'$ as $v \to c$. Thus, in the electron frame at rest $v = 0$, and, Eq. (11.425) becomes

$$\lambda' = 2\pi b \tag{11.426}$$

In the laboratory inertial frame for the case that $v = c$ in Eq. (11.425), λ is

$$\lambda = a \tag{11.427}$$

Thus, using Eqs. (11.426) and (11.427), the relativistic factor, γ^*, is

$$\gamma^* = \frac{\lambda}{\lambda'} = \frac{a}{2\pi b} \tag{11.428}$$

From Eqs. (11.417-11.419) and Eq. (11.428), the relativistic diamagnetic effect of the inverse integer radius of $H_2(1/p)$ compared to H_2, each with ellipsoidal MOs, is equivalent to the ratio of the semiminor and semimajor axes times the correction for the spherical orbital case given in Eq. (11.416). From the mass (Eq. (2.165)) and radius corrections (Eq. (2.163)) in Eq. (2.166), the relativistic stored magnetic energy contributes a factor γ_{SR} of

$$\gamma_{SR} = 2\pi\alpha\left(\frac{b}{a}\right)^2 = \pi\alpha \tag{11.429}$$

Thus, from Eqs. (11.401), (11.416), and (11.429), the relativistic change in flux, $\Delta\mathbf{B}_{SR}$, for the dihydrino molecule $H_2(1/p)$ is

$$\Delta\mathbf{B}_{SR} = -\gamma_{SR}\mu_0 A_2 \Delta\mathbf{m} = -\pi\alpha\mu_0 A_2 \Delta\mathbf{m} \tag{11.430}$$

Thus, using Eq. (11.411) and Eq. (11.430), the upfield chemical shift, $\frac{\Delta B_{SR}}{B}$, due to the relativistic effect of the molecule $H_2(1/p)$ corresponding to the lower-energy state with principal quantum energy state p is given by

$$\frac{\Delta B_{SR}}{B} = -\mu_0\pi\alpha\left(4-\sqrt{2}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{pe^2}{36a_0m_e} \tag{11.431}$$

The total shift, $\frac{\Delta B_T}{B}$, for $H_2(1/p)$ is given by the sum of that of H_2 given by Eq. (11.411) with $p=1$ plus that given by Eq. (11.431):

$$\frac{\Delta B_T}{B} = -\mu_0\left(4-\sqrt{2}\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}\right)\frac{e^2}{36a_0m_e}(1+\pi\alpha p) \tag{11.432}$$

$$\frac{\Delta B_T}{B} = -(28.01+0.64p)\,ppm \tag{11.433}$$

where $p = \text{integer} > 1$.

H_2 has been characterized by gas phase ^1H NMR. The experimental absolute resonance shift of gas-phase TMS relative to the proton's gyromagnetic frequency is -28.5 ppm [30]. H_2 was observed at 0.48 ppm compared to gas phase TMS set at 0.00 ppm [31]. Thus, the corresponding absolute H_2 gas-phase resonance shift of -28.0 ppm (-28.5 + 0.48) ppm was in excellent agreement with the predicted absolute gas-phase shift of -28.01 ppm given by Eq. (11.411).

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Section II

GENERAL DIATOMIC AND POLYATOMIC MOLECULAR IONS AND MOLECULES

Non-hydrogen diatomic and polyatomic molecular ions and molecules can be solved using the same principles as those used to solve hydrogen molecular ions and molecules wherein the hydrogen molecular orbitals (MOs) and hydrogen atomic orbitals serve as basis functions for the MOs of the general diatomic and polyatomic molecular ions or molecules. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of $\hbar$. Energy of the MO must be matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the atomic orbital (AO). In the case that an independent MO is formed, the AO force balance causes the remaining electrons to be at lower energy and a smaller radius. The atomic orbital may hybridize in order to achieve a bond at an energy minimum. At least one molecule or molecular ion representative of each of these cases was solved. Specifically, the results of the determination of bond parameters of H_3^+, D_3^+, OH, OD, H_2O, D_2O, NH, ND, NH_2, ND_2, NH_3, ND_3, CH, CD, CH_2, CH_3, CH_4, N_2, O_2, F_2, Cl_2, CN, CO, and NO are given in Table 13.1. The calculated results for homo- and hetero-diatomic radicals and molecules, and polyatomic molecular ions and molecules are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

TRIATOMIC MOLECULAR HYDROGEN-TYPE ION (H_3^+)

The polyatomic molecular ion $H_3^+(1/p)$ is formed by the reaction of a proton with a hydrogen-type molecule

$$H_2(1/p)+H^+ \rightarrow H_3^+(1/p) \tag{13.1}$$

and by the exothermic reaction

$$H_2^+(1/p)+H_2(1/p)\rightarrow H_3^+(1/p)+H(1/p) \tag{13.2}$$

FORCE BALANCE OF H_3^+-TYPE MOLECULAR IONS

$H_3^+(1/p)$-type molecular ions comprise two indistinguishable spin-paired electrons bound by three protons. The ellipsoidal molecular orbital (MO) satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. Since the protons are indistinguishable, ellipsoidal MOs about each pair of protons taken one at a time are indistinguishable. $H_3^+(1/p)$ is then given by a superposition or linear combinations of three equivalent ellipsoidal MOs that form a equilateral triangle where the points of contact between the prolate spheroids are equivalent in energy and charge density. The outer perimeter of the superposition of three prolate spheroids is the $H_3^+(1/p)$ MO with the protons at the foci that bind and maintain the electron MO.

As in the case for $H_2^+(1/p)$ and $H_2(1/p)$ shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section, the stability of $H_3^+(1/p)$ is due to the dependence of the charge density of the distance D from the origin to the tangent plane. That is,

$$D=\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}} \tag{13.3}$$

so that

$$\sigma=\frac{e}{4\pi ab^2}D \tag{13.4}$$

In other words, the surface density at any point on a charged ellipsoidal conductor is proportional to the perpendicular distance from the center of the ellipsoid to the plane tangent to the ellipsoid at the point. The charge is thus greater on the more sharply rounded ends farther away from the origin. This distribution places the charge closest to the protons to give a minimum energy.

The balanced forces also depend on D as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The D-dependence of the charge density as well as the centrifugal and Coulombic central field of two nuclei at the foci of the ellipsoid applies to each ellipsoid which is given from any other by a rotation of $|\phi|=\frac{\pi}{3}$ about an axis at a focus

that is perpendicular to the plane of the equilateral triangle defined by the three foci. Since the centrifugal, Coulombic, and magnetic forces relate mass and charge densities which are interchangeable by the ratio e/m_e, the conditions at any point on any given ellipsoid is applicable to any other point on the ellipsoid. Furthermore, this condition can be generalized to any point of the other members of the set of three ellipsoids due to equivalence. As a further constraint to maintain the force balance between the three protons and the $H_3^+(1/p)$ MO comprising the superposition of the three $H_2(1/p)$-type ellipsoidal MOs, the total charge of the two electrons must be normalized over the three basis set $H_2(1/p)$-type ellipsoidal MOs. In this case, the parameters of each basis element $H_2(1/p)$-type ellipsoidal MO is solved, and the energies are given by the electron charge where it appears multiplied by a factor of $3/2$ (three MOs normalized by the total charge of two electrons).

Consider each $H_2(1/p)$-type ellipsoidal MO. At each point on the $H_3^+(1/p)$ MO, the electron experiences a centrifugal force, and the balancing centripetal force (on each electron) is produced by the electric force between the electron and the ellipsoidal electric field and the radiation-reaction-type magnetic force between the two electrons causing the electrons to pair. The force balance equation derived in Force Balance of Hydrogen-Type Molecules section is given by Eq. (11.200):

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\varepsilon_o a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.5}$$

$$\frac{2a_0}{pa} - \frac{a_0}{pa} = 1 \tag{13.6}$$

$$a = \frac{a_0}{p} \tag{13.7}$$

Substitution of Eq. (13.7) into Eq. (11.79) is

$$c' = \frac{1}{p\sqrt{2}} a_0 \tag{13.8}$$

The internuclear distance given by multiplying Eq. (13.8) by two is

$$2c' = \frac{a_0\sqrt{2}}{p} \tag{13.9}$$

Substitution of Eqs. (13.7-13.8) into Eq. (11.80) is

$$b = c = \frac{1}{p\sqrt{2}} a_0 \tag{13.10}$$

Substitution of Eqs. (13.7-13.8) into Eq. (11.67) is

$$e=\frac{1}{\sqrt{2}} \tag{13.11}$$

Using the parameters given by Eqs. (13.7-13.11), the resulting $H_3^+(1/p)$ MO comprising the superposition of three $H_2(1/p)$-type ellipsoidal MOs is shown in Figure 6. The outer surface of the superposition comprises charge density of the MO. The equilateral triangular structure was confirmed experimentally [1]. The $H_3^+(1/p)$ MO having no distinguishable electrons is consistent with the absence of strong excited stated observed for H_3^+ [1]. It is also consistent with the absence of a permanent dipole moment [1].

ENERGIES OF H_3^+-TYPE MOLECULAR IONS

The due to the equivalence of the $H_2(1/p)$-type ellipsoidal MOs and the linear superposition of their energies, the energy components defined previously for the molecule, Eqs. (11.207-11.212) apply in the case of the corresponding $H_3^+(1/p)$ molecular ion. And, each molecular energy component is given by the integral of corresponding force in Eq. (13.5). Each energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set $H_2(1/p)$-type ellipsoidal MOs. Thus, the energies are those given for $H_2(1/p)$ in the Energies of Hydrogen-Type Molecules section with the electron charge, where it appears, multiplied by a factor of $3/2$. In addition, the three sets of equivalent proton-proton pairs give rise to a factor of three times the proton-proton repulsion energy given by Eq. (11.208). The parameters a and b are given by Eqs. (13.7) and (13.10), respectively.

$$V_e=\frac{3}{2}\frac{-2pe^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.12}$$

$$V_p=3\frac{p}{8\pi\varepsilon_0}\frac{e^2}{\sqrt{a^2-b^2}} \tag{13.13}$$

$$T=\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.14}$$

The energy, V_m, corresponding to the magnetic force of Eq. (13.5) is

$$V_m = \frac{3}{2}\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.15}$$

$$E_T = V_e + T + V_m + V_p \tag{13.16}$$

$$E_T = -\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(3p^2\sqrt{2}-p^2\sqrt{2}+3\frac{p^2\sqrt{2}}{4}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-3p^2\sqrt{2}\right] = -p^2 35.54975\ eV \tag{13.17}$$

where the charge e appears in the magnetic energy V_m according to Eqs. (7.14-7.24) as discussed in the Force Balance of Hydrogen-Type Molecules section.

VIBRATION OF H_3^+-TYPE MOLECULAR IONS

The vibrational energy levels of H_3^+-type molecular ions may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERM OF H_3^+-TYPE MOLECULAR IONS

As shown in the Vibration of Hydrogen-type Molecular Ions section, the electron orbiting the nuclei at the foci of an ellipse may be perturbed such that a stable reentrant orbit is established that gives rise to a vibrational state corresponding to time harmonic oscillation of the nuclei and electron. The perturbation is caused by a photon that is resonant with the frequency of oscillation of the nuclei wherein the radiation is electric dipole with the corresponding selection rules.

Oscillation may also occur in the transition state. The perturbation arises from the decrease in internuclear distance as the molecular bond forms. Relative to the unperturbed case given in the Force Balance of Hydrogen-type Molecular Ions section, the reentrant orbit may give rise to a decrease in the total energy while providing a transient kinetic energy to the vibrating nuclei. However, as an additional condition for stability, radiation must be considered. A nonradiative state must be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. The radiation reaction force due to the vibration of $H_2^+(1/p)$ and $H_2(1/p)$ in the transition state

was derived in the Doppler Energy Term of Hydrogen-type Molecular Ions section and the Doppler Energy Term of Hydrogen-type Molecules section, respectively, and corresponds to a Doppler energy, E_D, that is dependent on the motion of the electron and the nuclei. The radiation reaction force in the case of the vibration of $H_3^+(1/p)$ in the transition state also corresponds to the Doppler energy, E_D, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. Here, a nonradiative state must also be achieved after the emission due to transient vibration wherein the nonradiative condition given by Eq. (11.24) must be satisfied. Typically, a third body is required to form H_3^+-type molecular ions. For example, the exothermic chemical reaction of $H+H$ to form H_2 does not occur with the emission of a photon. Rather, the reaction requires a collision with a third body, M, to remove the bond energy- $H+H+M \rightarrow H_2+M^*$ [3]. The third body distributes the energy from the exothermic reaction, and the end result is the H_2 molecule and an increase in the temperature of the system. Thus, a third body removes the energy corresponding to the additional force term given by Eq. (11.180).

The kinetic energy of the transient vibration is derived from the corresponding central forces. From Eqs. (13.5) and (13.12), the central force terms between the electron MO and the protons of each of the three $H_2(1/p)$-type ellipsoidal MOs are

$$f(a) = -\frac{3}{2}\frac{pe^2}{4\pi\varepsilon_o a^2} \tag{13.18}$$

and

$$f'(a) = \frac{3}{2}\frac{2pe^2}{4\pi\varepsilon_o a^3} \tag{13.19}$$

Thus, using Eqs. (11.136) and (13.18-13.19), the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{3}{2}\frac{pe^2}{4\pi\varepsilon_o\left(\frac{a_0}{p}\right)^3}}{m_e}} = p^2 5.06326\,X\,10^{16}\ rad/s \tag{13.20}$$

where the semimajor axis, a, is $a = \frac{a_0}{p}$ according to Eq. (13.7). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar p^2 5.06326\,X\,10^{16}\ rad/s = p^2 33.3273\ eV \tag{13.21}$$

In Eq. (11.181), substitution of the total energy of the H_3^+-type molecular ion, E_T, (Eq. (13.17)) for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.21) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit.

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -35.54975p^2\ eV\sqrt{\frac{2e\left(p^2 33.3273\ eV\right)}{m_e c^2}} = -p^3 0.406013\ eV \quad (13.22)$$

The total energy of the H_3^+-type molecular ion is decreased by $\overline{E}_D$.

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of the H_3^+-type molecular ion given by Eq. (11.148). The decrease in the energy of the molecular ion due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ and $\overline{E}_{Kvib}$. Using Eq. (13.22) and the experimental vibrational energy H_3^+ of $E_{vib} = 2521.31\ cm^{-1} = 0.312605\ eV$ [1] gives

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar p^2\sqrt{\frac{k}{\mu}} \quad (13.23)$$

$$\overline{E}_{osc} = -p^3 0.406013\ eV + \frac{1}{2}p^2\left(0.312605\ eV\right) \quad (13.24)$$

The reentrant orbit for the binding of a proton to $H_2(1/p)$ causes two bonds to oscillate by increasing and decreasing in length along opposite sides of the equilateral triangle at a relative phase angle of 180°. Since the vibration and reentrant oscillation is along two lengths of the equilateral triangular MO with E symmetry, $\overline{E}_{osc}$ for $H_3^+(1/p)$, $\overline{E}_{osc}\left(H_3^+(1/p)\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left(H_3^+(1/p)\right) &= 2\left(\overline{E}_D + \frac{1}{2}\hbar p^2\sqrt{\frac{k}{\mu}}\right) \\ &= 2\left(-p^3 0.406013\ eV + \frac{1}{2}p^2\left(0.312605\ eV\right)\right)\end{aligned} \quad (13.25)$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies, $\overline{E}_K$, are the same independent of the isotope of hydrogen, but the vibrational

energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.22), Eq. (13.25), and the experimental vibrational energy D_3^+ of $E_{vib} = 1834.67\ cm^{-1} = 0.227472\ eV$ [1], the corresponding $\overline{E}_{osc}\left(D_3^+(1/p)\right)$ is

$$\overline{E}_{osc}\left(D_3^+(1/p)\right) = 2\left(-p^3\,0.406013\ eV + \frac{1}{2}p^2\left(0.227472\ eV\right)\right) \tag{13.26}$$

TOTAL AND BOND ENERGIES OF $H_3^+(1/p)$- AND $D_3^+(1/p)$-TYPE MOLECULAR IONS

The total energy of the $H_3^+(1/p)$-type molecular ion is given by the sum of E_T (Eqs. (13.16-13.17)) and $\overline{E}_{osc}\left(H_3^+(1/p)\right)$ given Eqs. (13.20-13.25). Thus, the total energy of $H_3^+(1/p)$ having a central field of $+pe$ at each focus of the prolate spheroid molecular orbital including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}\left(H_3^+(1/p)\right) \tag{13.27}$$

$$E_T = -p^2\left\{\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(3\sqrt{2}-\sqrt{2}+\frac{3\sqrt{2}}{4}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-3\sqrt{2}\right]\left[1+2p\sqrt{\frac{2\hbar\sqrt{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_o a_0^3}}}{m_e c^2}}\right]-2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\}$$
$$= -p^2\,35.54975 - 2p^3\,0.406013\ eV + 2p^2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{13.28}$$

From Eqs. (13.24-13.25) and (13.27-13.28), the total energy of the H_3^+-type molecular ion is

$$\begin{aligned} E_T &= -p^2\,35.54975\ eV + \overline{E}_{osc}\left(H_3^+(1/p)\right) \\ &= -p^2\,35.54975 - 2p^3\,0.406013\ eV + 2\left(\frac{1}{2}p^2\left(0.312605\ eV\right)\right) \\ &= -p^2\,35.23714\ eV - p^3\,0.812025\ eV \end{aligned} \tag{13.29}$$

The total energy of the D_3^+-type molecular ion is given by the sum of E_T (Eq. (13.17)) and $\overline{E}_{osc}\left(D_3^+(1/p)\right)$ given by Eq. (13.26):

$$E_T = -p^2 35.54975\ eV + \overline{E}_{osc}\left(D_3^+(1/p)\right)$$
$$= -p^2 35.54975 - 2p^3 0.406013\ eV + 2\left(\frac{1}{2}p^2(0.227472\ eV)\right) \quad (13.30)$$
$$= -p^2 35.32227\ eV - p^3 0.812025\ eV$$

The bond dissociation energy, E_D, is the difference between the total energy of the corresponding hydrogen molecule and E_T

$$E_D = E(H_2(1/p)) - E_T \quad (13.31)$$

where $E\left(H_2(1/p)\right)$ is given by Eq. (11.241):

$$E\left(H_2(1/p)\right) = -p^2 31.351\ eV - p^3 0.326469\ eV \quad (13.32)$$

and $E\left(D_2(1/p)\right)$ is given by Eq. (11.242):

$$E\left(D_2(1/p)\right) = -p^2 31.4345\ eV - p^3 0.326469\ eV \quad (13.33)$$

The H_3^+ bond dissociation energy, E_D, is given by Eqs. (13.31-13.32) and (13.29):

$$E_D = -p^2 31.351\ eV - p^3 0.326469\ eV - E_T$$
$$= -p^2 31.351\ eV - p^3 0.326469\ eV - \left(-p^2 35.23714\ eV - p^3 0.812025\ eV\right) \quad (13.34)$$
$$= p^2 3.88614\ eV + p^3 0.485556\ eV$$

The D_3^+ bond dissociation energy, E_D, is given by Eqs. (13.31), (13.33), and (13.30):

$$E_D = -p^2 31.4345\ eV - p^3 0.326469\ eV - E_T$$
$$= -p^2 31.4345\ eV - p^3 0.326469\ eV - \left(-p^2 35.32227\ eV - p^3 0.812025\ eV\right)$$
$$= p^2 3.88777\ eV + p^3 0.485556\ eV$$

(13.35)

THE H_3^+ MOLECULAR ION

FORCE BALANCE OF THE H_3^+ MOLECULAR ION

The force balance equation for H_3^+ is given by Eq. (13.5) where $p = 1$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_o a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D \quad (13.36)$$

which has the parametric solution given by Eq. (11.83) when

$$a = a_o \quad (13.37)$$

The semimajor axis, a, is also given by Eq. (13.7) where $p=1$. The internuclear distance, $2c'$, which is the distance between the foci is given by Eq. (13.9) where $p=1$.

$$2c' = \sqrt{2}a_o \tag{13.38}$$

The semiminor axis is given by Eq. (13.10) where $p=1$.

$$b = \frac{1}{\sqrt{2}}a_o \tag{13.39}$$

The eccentricity, e, is given by Eq. (13.11).

$$e = \frac{1}{\sqrt{2}} \tag{13.40}$$

ENERGIES OF THE H_3^+ MOLECULAR ION

The energies of H_3^+ are given by Eqs. (13.12-13.15) where $p=1$

$$V_e = \frac{3}{2}\frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -101.7538\ eV \tag{13.41}$$

$$V_p = 3\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 57.7245\ eV \tag{13.42}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 33.9179\ eV \tag{13.43}$$

The energy, V_m, of the magnetic force is

$$V_m = \frac{3}{2}\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -25.4384\ eV \tag{13.44}$$

The Doppler terms, $\overline{E}_{osc}\left(H_3^+(1/p)\right)$ and $\overline{E}_{osc}\left(D_3^+(1/p)\right)$ are given by Eqs. (13.25) and (13.26), respectively, where $p=1$

$$\begin{aligned}\overline{E}_{osc}\left(H_2^+\right) &= 2\left(\overline{E}_D + \overline{E}_{Kvib}\right)\\ &= 2\left(-0.406013\ eV + \frac{1}{2}(0.312605\ eV)\right)\\ &= -0.499420\ eV\end{aligned} \tag{13.45}$$

$$\begin{aligned}\overline{E}_{osc}\left(D_2\right) &= 2\left(-0.406013\ eV + \frac{1}{2}(0.227472\ eV)\right)\\ &= -0.584553\ eV\end{aligned} \tag{13.46}$$

The total energy, E_T, for H_3^+ given by Eqs. (13.27-13.29) is

$$E_T = -\left\{\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(3\sqrt{2}-\sqrt{2}+\frac{3\sqrt{2}}{4}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-3\sqrt{2}\right]\left[1+2\sqrt{\frac{2\hbar\sqrt{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_o a_0^3}m_e}}{m_e c^2}}\right]-2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\}$$

$$=-35.54975-2(0.406013\ eV)+2\left(\frac{1}{2}(0.31260516\ eV)\right)$$

$$=-36.049167\ eV \tag{13.47}$$

From Eqs. (13.27-13.28) and (13.30), the total energy, E_T, for D_3^+ is

$$E_T = -35.54975-2(0.406013\ eV)+2\left(\frac{1}{2}(0.227472\ eV)\right) \tag{13.48}$$

$$=-36.134300\ eV$$

The bond dissociation energy, E_D, is the difference between the total energy of H_2 or D_2 and E_T. The H_3^+ molecular bond dissociation energy, E_D, given by the difference between the experimental total energy of H_2 [5-7] [1] and the total energy of H_3^+ (Eqs. (13.29) where $p=1$ and (13.47)) is

$$E_D = -31.675\ eV\ -(-36.049167\ eV) \tag{13.49}$$

$$=4.374167\ eV$$

The H_3^+ bond dissociation energy, E_D, given by Eq. (13.34) where $p=1$ is

$$E_D = 3.88614\ eV+0.485556\ eV \tag{13.50}$$

$$=4.37170\ eV$$

The experimental bond dissociation energy of H_3^+ [8] is

$$E_D = 4.373\ eV \tag{13.51}$$

The difference between the results of Eqs. (13.49) and (13.50) is within the experimental and propagated errors in the different calculations. The calculated results are based on first principles and given in closed-form equations containing fundamental constants only. The agreement between the experimental and calculated results for the H_3^+ bond dissociation energy is excellent.

[1] The experimental total energy of the hydrogen molecule is given by adding the first (15.42593 eV) [5] and second (16.2494 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the hydrogen atom (13.59844 eV) [6] and the bond energy of H_2^+ (2.651 eV) [7].

The predicted D_3^+ molecular bond dissociation energy, E_D, given by the difference between the total energy of D_3^+ (Eqs. (13.30) where $p=1$ and (13.48)) and the experimental total energy of D_2 [9-10][2] is

$$\begin{aligned} E_D &= -31.76\ eV - (-36.134300\ eV) \\ &= 4.374300\ eV \end{aligned} \tag{13.52}$$

The D_3^+ bond dissociation energy, E_D, given by Eq. (13.35) where $p=1$ is

$$\begin{aligned} E_D &= 3.88777\ eV + 0.485556\ eV \\ &= 4.373331\ eV \end{aligned} \tag{13.53}$$

The results of the determination of bond parameters of H_3^+ are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

HYDROXYL RADICAL (OH)

The water molecule can be solved by first considering the solution of the hydroxyl radical which is formed by the reaction of a hydrogen atom and an oxygen atom:

$$H + O \rightarrow OH \tag{13.54}$$

The hydroxyl radical OH can be solved using the same principles as those used to solve the hydrogen molecule wherein the diatomic molecular orbital (MO) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serves as basis function in linear combination with an oxygen atomic orbital (AO) to form the MO of OH. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of $\hbar$. A further constraint with the substitution of a heteroatom (O) for one of the hydrogen atoms is that the constant energy of the MO must match the energy of the heteroatom.

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[2] The experimental total energy of the deuterium molecule is given by adding the first (15.466 eV) [9] and second (16.294 eV) ionization energies where the second ionization energy is given by the addition of the ionization energy of the deuterium atom (13.603 eV) [10] and the bond energy of D_2^+ (2.692 eV) [9].

FORCE BALANCE OF OH

OH comprises two spin-paired electrons in a chemical bond between the oxygen atom and the hydrogen atom such that one electron on O remains unpaired. The OH radical MO is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal H_2 MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the H-atom electron forms a H_2-type ellipsoidal MO with one of the O-atom electrons. The O electron configuration given in the Eight-Electron Atoms section is $1s^2 2s^2 2p^4$, and the orbital arrangement is

$$\begin{array}{c} \text{2p state} \\ \underline{\uparrow\downarrow} \quad \underline{\uparrow} \quad \underline{\uparrow} \\ 1 \quad 0 \quad -1 \end{array} \tag{13.55}$$

corresponding to the ground state ${}^3P_2$.

In determining the central forces for O in the Radius and Ionization Energy of the Outer Electron of the Oxygen Atom section, it was shown that the energy is minimized with conservation of angular momentum by the cancellation of the orbital angular momentum of a p_x electron by that of the p_y electron with the pairing of electron eight to fill the p_x orbital. Then, the diamagnetic force is given by Eq. (10.156) is that of atomic nitrogen (Eq. (10.136) corresponding to the p_z-orbital electron (Eq. (10.82) with $m=0$) as the source of diamagnetism with an additional contribution from the uncanceled p_x electron (Eq. (10.82) with $m=1$). From Eqs. (10.83) and (10.89), the paramagnetic force, $\mathbf{F}_{mag\ 2}$, is given by Eq. (10.157) corresponding to the spin-angular-momentum contribution alone of the p_x electron and the orbital angular momentum of the p_z electron, respectively. The diamagnetic and paramagnetic forces cancel such that the central force is purely the Coulombic force. This central force is maintained with bond formation such that the energy of the $O2p$ shell is unchanged. Thus, the angular momentum of each electron of the $O2p$ shell is conserved with bond formation. The central paramagnetic force due to spin is provided by the spin-pairing force of the OH MO that has the symmetry of an s orbital that superimposes with the $2p$ orbitals such that the corresponding angular momenta of the $O2p$ orbitals are unchanged.

The $O2p_y$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the H atom is along the internuclear axis. Due to symmetry, the other O electrons

are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the OH MO involve only the $O2p_y$ and $H1s$ electrons and the change in the magnetic energy of the $O2p_y$ electron with the other O electrons (Eq. (13.152)) with the formation of the OH MO. The forces are determined by these energies.

As in the case of H_2, the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into O atom for distances shorter than the radius of the $2p$ shell. Otherwise, the electric field of the other $O2p$ electrons would be perturbed, and the $2p$ shell would not be stable. The corresponding increase in energy of O would not be offset by any energy decrease in the OH MO based on the distance from the O nucleus to the $H1s$ electron compared to those of the $O2p$ electrons. Thus, the MO surface comprises a prolate spheroid at the H proton that is continuous with the $2p$ shell at the O atom. The energy of the prolate spheroid is matched to that of the $O2p$ shell.

The orbital energy E for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic T and potential V energies. $E=T+V$ is constant, and the closed orbits are those for which $T<|V|$, and the open orbits are those for which $T\geq|V|$. It can be shown that the time average of the kinetic energy, $<T>$, for elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, $|<V>|$. $<T>=1/2|<V>|$ [11]. In the case of an atomic orbital (AO), $E=T+V$, and for all points on the AO, $|E|=T=1/2|V|$. As shown in the Hydrogen-type Molecular Ions section, each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptic plane cross section of the spheroidal MO through the foci. The motion is such that eccentric angle, θ, changes at a constant rate at each point. That is $\theta=\omega t$ at time t where ω is a constant, and

$$r(t)=\mathbf{i}a\cos\omega t+\mathbf{j}b\sin\omega t \tag{13.56}$$

Consider the boundary condition that the MO of OH comprises a linear combination of an oxygen AO and a H_2-type ellipsoidal MO. The charge density of H_2-type ellipsoidal MO given by Eq. (13.4) maintains that the surface is an equipotential; however, the potential and kinetic energy of a point on the surface changes as it orbits the central field. The potential energy is a maximum and the kinetic energy is a minimum at the semimajor axis, and the reverse occurs at the semiminor axis. Since the time average of the kinetic energy, $<T>$, for

elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, by symmetry, the $<T>=1/2<|V|>$ condition holds for 1/2 of the H_2-type ellipsoidal MO having the H focus and ending at the plane defined by the semiminor axes. The O nucleus comprises the other focus of the OH MO. The $O2p$ AO obeys the energy relationship for all points. Thus, the linear combination of the H_2-type ellipsoidal MO with the $O2p$ AO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $O2p$ AO in order to match the energy relationships. Thus, the OH MO must comprise 75% of a H_2-type ellipsoidal MO (1/2 +25%) and an oxygen AO:

$$1\ O2p_y\ AO + 0.75\ H_2\ MO \rightarrow OH\ MO \tag{13.57}$$

The force balance of the OH MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.57). The force constant k of a H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by Eq. (11.65):

$$k = \frac{2e^2}{4\pi\varepsilon_o} \tag{13.58}$$

Since the H_2-type ellipsoidal MO comprises 75% of the OH MO, the electron charge density in Eq. (13.58) is given by $-0.75e$. Thus, k' of the H_2-type-ellipsoidal-MO component of the OH MO is

$$k' = \frac{(0.75)2e^2}{4\pi\varepsilon_0} \tag{13.59}$$

L for the electron equals $\hbar$; thus, the distance from the origin of the OH MO to each focus c' is given by Eqs. (11.79) and (13.59):

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 1.5a}} = \sqrt{\frac{2aa_0}{3}} \tag{13.60}$$

The internuclear distance from Eq. (13.60) is

$$2c' = 2\sqrt{\frac{2aa_0}{3}} \tag{13.61}$$

The length of the semiminor axis of the prolate spheroidal OH MO $b=c$ given by Eq. (11.80) is

$$b=\sqrt{a^2-c'^2} \tag{13.62}$$

The eccentricity, e, is

$$e=\frac{c'}{a} \tag{13.63}$$

Then, the solution of the semimajor axis a allows for the solution of the other axes of the prolate spheroidal and eccentricity of the OH MO.

The general equation of the ellipsoidal MO having semiprincipal axes a, b, c given by

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{c^2}=1 \tag{13.64}$$

is also completely determined by the total energy E given by Eq. (11.18):

$$r=\frac{m\frac{L^2}{m^2}k^{-1}}{1+\left(1+2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta} \tag{13.65}$$

The energy of the oxygen $2p$ shell is the negative of the ionization energy of the oxygen atom given by Eq. (10.163). Experimentally, the energy is [12]

$$E(2p\ shell)=-E(ionization;\ O)=-13.6181\ eV \tag{13.66}$$

Since the prolate spheroidal MO transitions to the O AO, the energy E in Eq. (13.66) adds to that of the H_2-type ellipsoidal MO to give the total energy of the OH MO. From the energy equation and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the OH MO are solved.

The energy components derived previously for the hydrogen molecule, Eqs. (11.207-11.212), apply in the case of the H_2-type ellipsoidal MO. As in the case of the energies of $H_3^+(1/p)$ given by Eqs. (13.12-13.16), each energy component of the H_2-type ellipsoidal MO is the total for the two equivalent electrons with the exception that the total charge and energies of the two electrons is normalized by the percentage composition given by Eq. (13.57):

$$V_e=\left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.67}$$

$$V_p=\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \tag{13.68}$$

$$T=\left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.69}$$

$$V_m=\left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{13.70}$$

$$E_T=V_e+T+V_m+V_p \tag{13.71}$$

$$E_T=-\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\left[\left(\frac{3}{2}-\frac{3}{4}\frac{a_0}{a}+\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right] \tag{13.72}$$

$$E_T=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \tag{13.73}$$

Since the prolate spheroidal MO transitions to the O AO and the energy of the $O2p$ shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.66), the total energy $E_T(OH)$ of the OH MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the O AO and the H_2-type ellipsoidal MO that forms the OH MO as given by Eq. (13.57):

$$\begin{aligned}E_T(OH)&=E_T+E(2p\ shell)\\&=E_T-E(ionization;\ O)\\&=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV\end{aligned} \tag{13.74}$$

To match the boundary condition that the total energy of the entire the H_2-type ellipsoidal MO is given by Eq. (11.212):

$$E_T(H_2)=-\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]=-31.63536831\ eV \tag{13.75}$$

$E_T(OH)$ given by Eq. (13.74) is set equal to Eq. (13.75):

$$E_T(OH)=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV=-31.63536831\ eV$$

(13.76)

From the energy relationship given by Eq. (13.76) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the OH MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.76) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e18.01726831 \tag{13.77}$$

The most convenient way to solve Eq. (13.77) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.26430a_0=6.69039\,X\,10^{-11}\ m \tag{13.78}$$

Substitution of Eq. (13.78) into Eq. (13.60) gives

$$c'=0.91808a_0=4.85826\,X\,10^{-11}\ m \tag{13.79}$$

The internuclear distance given by multiplying Eq. (13.79) by two is

$$2c'=1.83616a_0=9.71651\,X\,10^{-11}\ m \tag{13.80}$$

The experimental bond distance is [13]

$$2c'=9.71\,X\,10^{-11}\ m \tag{13.81}$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.62) gives

$$b=c=0.86925a_0=4.59985\,X\,10^{-11}\ m \tag{13.82}$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.63) gives

$$e=0.72615 \tag{13.83}$$

The nucleus of the H atom and the nucleus of the O atom comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $O2p_y$ AO can be determined from the polar equation of the ellipse (Eq. (11.10)):

$$r=r_0\frac{1+e}{1+e\cos\theta'} \tag{13.84}$$

The radius of the $O2p_y$ AO given by Eq. (10.162) is $r_8=a_0$, and the polar radial coordinate of the ellipse and the radius of the $O2p_y$ AO are equal at the point of intersection. Thus, Eq. (13.84) becomes

$$a_0=(a-c')\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'} \tag{13.85}$$

such that the polar angle θ' is given by

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{a_0}-1\right)\right) \tag{13.86}$$

Substitution of Eqs. (13.78-13.79) into Eq. (13.86) gives

$$\theta' = 123.65° \tag{13.87}$$

Then, the angle θ_{O2p_yAO} the radial vector of the $O2p_y$ AO makes with the internuclear axis is

$$\theta_{O2p_yAO} = 180° - 123.65° = 56.35° \tag{13.88}$$

as shown in Figure 7.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the O radial vector obeys the following relationship:

$$a_0 \sin\theta_{O2p_yAO} = b \sin\theta_{H_2MO} \tag{13.89}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{a_0 \sin 56.35°}{b} \tag{13.90}$$

with the use of Eq. (13.88). Substitution of Eq. (13.82) into Eq. (13.90) gives

$$\theta_{H_2MO} = 73.27° \tag{13.91}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.92}$$

Substitution of Eqs. (13.78) and (13.91) into Eq. (13.92) gives

$$d_{H_2MO} = 0.36397a_0 = 1.92606\,X\,10^{-11}\ m \tag{13.93}$$

The distance d_{O2pAO} along the internuclear axis from the origin of the O atom to the point of intersection of the orbitals is given by

$$d_{O2pAO} = c' - d_{H_2MO} \tag{13.94}$$

Substitution of Eqs. (13.79) and (13.93) into Eq. (13.94) gives

$$d_{O2pAO} = 0.55411a_0 = 2.93220\,X\,10^{-11}\ m \tag{13.95}$$

As shown in Eq. (13.57), in addition to the p-orbital charge-density modulation, the uniform charge-density in the p_y orbital is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25. The internuclear axis of the $O-H$ bond is perpendicular to the bonding p_y orbital. Using the orbital composition of OH (Eq. (13.57)), the radii of $O1s = 0.12739a_0$ (Eq. (10.51)), $O2s = 0.59020a_0$ (Eq. (10.62)), and $O2p = a_0$ (Eq. (10.162)) shells, and the parameters of the OH MO given by Eqs. (13.3-13.4), (13.78-13.80), (13.82-13.83), and (13.87-13.95), the dimensional diagram and charge-density of the OH MO comprising the linear combination of the H_2-type ellipsoidal MO and the O AO according to Eq. (13.57) are shown in Figures 7 and 8, respectively.

ENERGIES OF OH

The energies of OH given by the substitution of the semiprincipal axes (Eqs. (13.78-13.80) and (13.82)) into the energy equations (Eqs. (13.67-13.73)) are

$$V_e = \left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -40.92709\ eV \tag{13.96}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 14.81988\ eV \tag{13.97}$$

$$T = \left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 16.18567\ eV \tag{13.98}$$

$$V_m = \left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -8.09284\ eV \tag{13.99}$$

$$E_T(OH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - 13.6181\ eV = -31.63247\ eV \tag{13.100}$$

where $E_T(OH)$ is given by Eq. (13.74) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

VIBRATION AND ROTATION OF OH

The vibrational energy of OH may be solved in the same manner as that of hydrogen-type molecular ions and hydrogen molecules given in the Vibration of Hydrogen-type Molecular Ions section, and the Vibration of Hydrogen-type Molecules section, respectively, except that the orbital composition and the requirement that the $O2p$ shell remain at the same energy and

radius in the OH MO as it is in the O atom must be considered. Each p-orbital comprises the sum of a constant function and a spherical harmonic function as given by Eq. (1.65). In addition to the p-orbital charge-density modulation, the uniform charge-density in p_y orbital is increased by a factor of 0.25, and the H-atom electron density is decreased by a factor of 0.25. The force between the electron density of the H_2-type ellipsoidal MO and the nuclei determines the vibrational energy. With the radius of the orbit at the oxygen atom fixed at

$$r_8 = a_0 \tag{13.101}$$

according to Eq. (10.162), the central-force terms for the reentrant orbit between the electron density and the nuclei of the H_2-type ellipsoidal MO are given by Eqs. (11.213-11.214), except that the corresponding charge of $-0.75e$ replaces the charge of $-e$ of Eqs. (11.213-11.214). Furthermore, due to condition that the $O2p$ shell remain at the same energy and radius in the OH MO as it is in the O atom, the oscillation of H_2-type ellipsoidal is along the semiminor axis with the apsidal angle of Eq. (11.140) given by $\psi = \pi$. Thus, the semimajor axis a of Eqs. (11.213-11.214) is replaced by the semiminor axis b:

$$f(b) = -\frac{0.75e^2}{8\pi\varepsilon_0 b^2} \tag{13.102}$$

and

$$f'(b) = \frac{0.75e^2}{4\pi\varepsilon_0 b^3} \tag{13.103}$$

Here, the force factor of 0.75 is equal to the equivalent term of Eq. (13.59). As the H_2-type ellipsoidal oscillates along b, the internuclear distance changes 180° out of phase. Thus, the distance for the reactive nuclear-repulsive terms is given by internuclear distance $2c'$ (Eq. (13.80)). Similar to that of Eqs. (11.215-11.216), the contribution from the repulsive force between the two nuclei is

$$f(2c') = \frac{e^2}{8\pi\varepsilon_0 (2c')^2} \tag{13.104}$$

and

$$f'(2c') = -\frac{e^2}{4\pi\varepsilon_0 (2c')^3} \tag{13.105}$$

Thus, from Eqs. (11.136), (11.213-11.217), and (13.102-13.105), the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 b^3} - \frac{e^2}{8\pi\varepsilon_0 (2c')^3}}{\mu}}$$
$$= \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 (0.86925a_0)^3} - \frac{e^2}{8\pi\varepsilon_0 (1.83616a_0)^3}}{\frac{16}{17}m_p}} \quad (13.106)$$
$$= 6.96269\,X\,10^{14}\ rad/s$$

where b is given by Eq. (13.82), $2c'$ is given by Eq. (13.80), and the reduced mass of ^{16}OH is given by:

$$\mu_{^{16}OH} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(16)}{1+16} m_p \quad (13.107)$$

where m_p is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for ^{16}OH given by Eqs. (11.136), (11.148), and (13.106) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{763.18\ Nm^{-1}}{\mu}} = 6.96269\,X\,10^{14}\ radians/s \quad (13.108)$$

where the reduced nuclear mass of ^{16}OH is given by Eq.(13.107) and the spring constant, $k(0)$, given by Eqs. (11.136) and (13.106) is

$$k(0) = 763.18\ Nm^{-1} \quad (13.109)$$

The ^{16}OH transition-state vibrational energy, $E_{vib}(0)$, given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \hbar\omega = \hbar 6.96269\,X\,10^{14}\ rad/s = 0.4583\ eV = 3696.38\ cm^{-1} \quad (13.110)$$

Zero-order or zero-point vibration is not physical and is not observed experimentally as discussed in the Diatomic Molecular Vibration section; yet, there is a term ω_e of the old point-particle-probability-wave-mechanics that can be compared to $E_{vib}(0)$. From Herzberg [14], ω_e, from the experimental curve fit of the vibrational energies of ^{16}OH is

$$\omega_e = 3735.21\ cm^{-1} \quad (13.111)$$

As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and

expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods. The energy $\tilde{\nu}_\upsilon$ of state υ is

$$\tilde{\nu}_\upsilon = \upsilon\omega_0 - \upsilon(\upsilon-1)\omega_0 x_0, \quad \upsilon = 0,1,2,3... \tag{13.112}$$

where

$$\omega_0 x_0 = \frac{hc\omega_0^2}{4D_0} \tag{13.113}$$

ω_0 is the frequency of the $\upsilon = 1 \rightarrow \upsilon = 0$ transition, and D_0 is the bond dissociation energy given by Eq. (13.162). From Eq. (13.112), ω_0 is given by

$$\omega_0 = E_{vib}(0) - 2\omega_0 x_0 \tag{13.114}$$

Substitution of Eq. (13.113) into Eq. (13.114) gives

$$\omega_0 = E_{vib}(0) - 2\frac{hc\omega_0^2}{4D_0} \tag{13.115}$$

Eq. (13.115) can be expressed as

$$\omega_0^2 + \frac{2D_0}{hc}\omega_0 - \frac{2D_0}{hc}E_{vib}(0) = 0 \tag{13.116}$$

which can be solved by the quadratic formula:

$$\omega_0 = \frac{-\frac{2D_0}{hc} \pm \sqrt{\left(\frac{2D_0}{hc}\right)^2 + 4\frac{2D_0}{hc}E_{vib}(0)}}{2} \tag{13.117}$$

Only the positive root is real, physical; thus,

$$\begin{aligned}\omega_0\left(cm^{-1}\right) &= \frac{-\frac{2D_0}{100hc} + \sqrt{\left(\frac{2D_0}{100hc}\right)^2 + 4\frac{2D_0}{100hc}E_{vib}(0)}}{2} \\ &= \frac{-\frac{2e(4.4104\ eV)}{100hc} + \sqrt{\left(\frac{2e(4.4104\ eV)}{100hc}\right)^2 + 4\frac{2e(4.4104\ eV)}{100hc}\left(3696.37\ cm^{-1}\right)}}{2} \\ &= 3522.02\ cm^{-1}\end{aligned} \tag{13.118}$$

where $E_{vib}(0)$ is given by Eq. (13.110) and D_0 is given by Eq. (13.156). The corresponding ^{16}OH $\upsilon = 1 \rightarrow \upsilon = 0$ vibrational energy, $E_{vib}(1)$, in electron volts is:

$$E_{vib}(1) = 0.43666\ eV \tag{13.119}$$

The experimental vibrational energy of ^{16}OH is [16-17]

$$E_{vib}(1) = 0.4424\ eV \qquad (3568\ cm^{-1}) \tag{13.120}$$

Using Eqs. (13.118-13.119) with Eq. (13.113), the anharmonic perturbation term, $\omega_0 x_0$, of ^{16}OH is

$$\omega_0 x_0 = \frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}0.43666\ eV\right)^2}{4e(4.4104\ eV)} cm^{-1} = 87.18\ cm^{-1} \tag{13.121}$$

The experimental anharmonic perturbation term, $\omega_0 x_0$, of ^{16}OH [14] is

$$\omega_0 x_0 = 82.81\ cm^{-1} \tag{13.122}$$

The vibrational energies of successive states are given by Eqs. (13.110), (13.112), and (13.121).

Using the reduced nuclear mass of ^{16}OD given by

$$\mu_{^{16}OD} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(16)}{2+16} m_p \tag{13.123}$$

where m_p is the proton mass, the corresponding parameters for deuterated hydroxyl radical ^{16}OD (Eqs. (13.102-13.121) and (13.162)) are

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{763.18\ Nm^{-1}}{\mu}} = 5.06610\ X\ 10^{14}\ radians/s \tag{13.124}$$

$$k(0) = 763.18\ Nm^{-1} \tag{13.125}$$

$$E_{vib}(0) = \hbar\omega = \hbar 5.06610\ X\ 10^{14}\ rad/s = 0.33346\ eV = 2689.51\ cm^{-1} \tag{13.126}$$

$$\omega_0\left(cm^{-1}\right)=\frac{-\frac{2D_0}{100hc}+\sqrt{\left(\frac{2D_0}{100hc}\right)^2+4\frac{2D_0}{100hc}E_{vib}(0)}}{2}$$

$$=\frac{-\frac{2e(4.4687\ eV)}{100hc}+\sqrt{\left(\frac{2e(4.4687\ eV)}{100hc}\right)^2+4\frac{2e(4.4687\ eV)}{100hc}\left(2689.51\ cm^{-1}\right)}}{2}$$

$$=2596.02\ cm^{-1} \tag{13.127}$$

$$E_{vib}(1)=0.3219\ eV \tag{13.128}$$

$$\omega_0 x_0=\frac{100hc\left(8.06573X10^3\ \frac{cm^{-1}}{eV}0.3219\ eV\right)^2}{4e(4.4687\ eV)}cm^{-1}=46.75\ cm^{-1} \tag{13.129}$$

From Herzberg [14], ω_e, from the experimental curve fit of the vibrational energies of ^{16}OD is

$$\omega_e=2720.9\ cm^{-1} \tag{13.130}$$

The experimental vibrational energy of ^{16}OD is [16-17]

$$E_{vib}(1)=0.3263\ eV \qquad \left(2632.1\ cm^{-1}\right) \tag{13.131}$$

and the experimental anharmonic perturbation term, $\omega_0 x_0$, of ^{16}OD [14] is

$$\omega_0 x_0=44.2\ cm^{-1} \tag{13.132}$$

which match the predictions given by Eqs. (13.126), (13.127-13.128), and (13.129), respectively.

The B_e rotational parameters for ^{16}OH and ^{16}OD are given by Eq. (12.65):

$$B_e=\frac{\hbar^2}{2I_e hc} \tag{13.133}$$

where

$$I=\mu r^2 \tag{13.134}$$

Using the internuclear distance, $r=2c'$, and reduced mass of ^{16}OH given by Eqs. (13.80) and (13.107), respectively, the corresponding B_e is

$$B_e=18.835\ cm^{-1} \tag{13.135}$$

The experimental B_e rotational parameter of ^{16}OH is [14]

$$B_e = 18.871\ cm^{-1} \tag{13.136}$$

Using the internuclear distance, $r = 2c'$, and reduced mass of ^{16}OD given by Eqs. (13.80) and (13.123), respectively, the corresponding B_e is

$$B_e = 9.971\ cm^{-1} \tag{13.137}$$

The experimental B_e rotational parameter of ^{16}OD is [14]

$$B_e = 10.01\ cm^{-1} \tag{13.138}$$

THE DOPPLER ENERGY TERMS OF ^{16}OH AND ^{16}OD

The radiation reaction force in the case of the vibration of ^{16}OH in the transition state corresponds to the Doppler energy, E_D, given by Eq. (11.181) and Eq. (13.22) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. Following the same consideration as those used to derive Eqs. (13.102-13.103) and Eqs. (11.231-11.232), the central force terms between the electron density and the nuclei of ^{16}OH MO with the radius of the orbit at the oxygen atom fixed at

$$r_8 = a_0 \tag{13.139}$$

according to Eq. (10.162) are

$$f(b) = -\frac{0.75e^2}{4\pi\varepsilon_0 b^2} \tag{13.140}$$

and

$$f'(b) = \frac{(0.75)2e^2}{4\pi\varepsilon_0 b^3} \tag{13.141}$$

wherein the oscillation of H_2-type ellipsoidal MO is along the semiminor axis b with the apsidal angle of Eq. (11.140) given by $\psi = \pi$ due to condition that the $O2p$ shell remain at the same energy and radius in the OH MO as it is in the O atom. Thus, using Eqs. (11.136) and (13.140-13.141), the angular frequency of this oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 4.41776\,X\,10^{16}\ rad/s \tag{13.142}$$

The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 4.41776\, X\, 10^{16}\ rad/s = 29.07844\ eV \tag{13.143}$$

In Eq. (11.181), substitution of the total energy of OH, $E_T(OH)$, (Eq. (13.76)) for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.143) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit.

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(29.07844\ eV)}{m_e c^2}} = -0.33749\ eV \tag{13.144}$$

The total energy of OH is decreased by $\overline{E}_D$.

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of OH given by Eq. (13.120). The decrease in the energy of the OH due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ and $\overline{E}_{Kvib}$. Using Eq. (13.144) and the experimental ^{16}OH ω_e of 3735.21 cm^{-1} $(0.463111\ eV)$ [16-17] gives

$$\overline{E}_{osc}(^{16}OH) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.145}$$

$$\overline{E}_{osc}(^{16}OH) = -0.33749\ eV + \frac{1}{2}(0.463111\ eV) = -0.10594\ eV \tag{13.146}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies, $\overline{E}_K$, are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.144), Eqs. (13.145-13.146), and the experimental ^{16}OD ω_e of 2720.9 cm^{-1} $(0.33735\ eV)$ [16-17], the corresponding $\overline{E}_{osc}(^{16}OD)$ is

$$\overline{E}_{osc}(^{16}OD) = -0.33749\ eV + \frac{1}{2}(0.33735\ eV) = -0.16881\ eV \tag{13.147}$$

TOTAL AND BOND ENERGIES OF ^{16}OH AND ^{16}OD RADICALS

$E_{T+osc}\left(^{16}OH\right)$, the total energy of the ^{16}OH radical including the Doppler term, is given by the sum of $E_T\left(OH\right)$ (Eq. (13.76)) and $\overline{E}_{osc}\left(^{16}OH\right)$ given by Eqs. (13.142-13.146):

$$\begin{aligned} E_{T+osc}\left(^{16}OH\right) &= V_e + T + V_m + V_p + E\left(2p\ shell\right) + \overline{E}_{osc}\left(^{16}OH\right) \\ &= E_T\left(OH\right) + \overline{E}_{osc}\left(^{16}OH\right) \end{aligned} \tag{13.148}$$

$$\begin{aligned} E_{T+osc}\left(^{16}OH\right) &= \left\{\frac{-e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV\right\}\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}{m_e c^2}}\right]+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \\ &= -31.63537\ eV - 0.33749\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.149}$$

From Eqs. (13.145-13.146) and (13.148-13.149), the total energy of ^{16}OH is

$$\begin{aligned} E_{T+osc}\left(^{16}OH\right) &= -31.63537\ eV + \overline{E}_{osc}\left(^{16}OH\right) \\ &= -31.63537\ eV - 0.33749\ eV + \frac{1}{2}\left(0.463111\ eV\right) \\ &= -31.74130\ eV \end{aligned} \tag{13.150}$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left(^{16}OD\right)$, the total energy of ^{16}OD including the Doppler term, is given by the sum of $E_T\left(OD\right) = E_T\left(OH\right)$ (Eq. (13.76)) and $\overline{E}_{osc}\left(^{16}OD\right)$ given by Eq. (13.147):

$$\begin{aligned} E_{T+osc}\left(^{16}OD\right) &= -31.63537\ eV + \overline{E}_{osc}\left(^{16}OD\right) \\ &= -31.63537\ eV - 0.33749\ eV + \frac{1}{2}\left(0.33735\ eV\right) \\ &= -31.80418\ eV \end{aligned} \tag{13.151}$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. The dissociation of the bond of the hydroxyl radical forms a free hydrogen atom with one unpaired electron and an oxygen atom with two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_o\mu_B^2}{a_0^3} = 0.114411\ eV \tag{13.152}$$

The corresponding bond dissociation energy, E_D, is given by the sum of the total energies of the oxygen atom and the corresponding hydrogen atom minus the sum of $E_{T+osc}\left(^{16}OH\right)$ and $E(magnetic)$:

$$E_D = E(^{16}O) + E(H) - E_{T+osc}\left(^{16}OH\right) - E\left(magnetic\right) \tag{13.153}$$

$E(^{16}O)$ is given by Eq. (13.66), $E_D(H)$ [18] is

$$E(H) = -13.59844\ eV \tag{13.154}$$

and $E_D(D)$ [19] is

$$E(D) = -13.603\ eV \tag{13.155}$$

The ^{16}OH bond dissociation energy, $E_D\left(^{16}OH\right)$, is given by Eqs. (13.150) and (13.152-13.155):

$$\begin{aligned} E_D\left(^{16}OH\right) &= -\left(13.6181\ eV + 13.59844\ eV\right) - \left(E\left(magnetic\right) + E_{T+osc}\left(^{16}OH\right)\right) \\ &= -27.21654\ eV - \left(0.114411\ eV - 31.74130\ eV\right) \\ &= 4.4104\ eV \end{aligned} \tag{13.156}$$

The experimental ^{16}OH bond dissociation energy is [20]

$$E_D\left(^{16}OH\right) = 4.41174\ eV \tag{13.157}$$

The ^{16}OD bond dissociation energy, $E_D\left(^{16}OD\right)$, is given by Eqs. (13.151-13.153):

$$\begin{aligned} E_D\left(^{16}OD\right) &= -\left(13.6181\ eV + 13.603\ eV\right) - \left(E\left(magnetic\right) + E_{T+osc}\left(^{16}OD\right)\right) \\ &= -27.2211\ eV - \left(0.114411\ eV - 31.804183\ eV\right) \\ &= 4.4687\ eV \end{aligned} \tag{13.158}$$

The experimental ^{16}OD bond dissociation energy is [21-22]

$$E_D\left(^{16}OD\right) = 4.454\ eV \tag{13.159}$$

The results of the determination of bond parameters of OH and OD are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

WATER MOLECULE (H_2O)

The water molecule H_2O is formed by the reaction of a hydrogen atom with a hydroxyl radical:

$$OH + H \rightarrow H_2O \tag{13.160}$$

The water molecule can be solved using the same principles as those used to solve the hydrogen molecule, H_3^+, and OH wherein the diatomic molecular orbital (MO) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serves as basis function in a linear combination with an oxygen atomic orbital (AO) to form the MO of H_2O. The solution is very similar to that of OH except that there are two OH bonds in water.

FORCE BALANCE OF H_2O

H_2O comprises two chemical bonds between oxygen and hydrogen. Each $O-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the oxygen atom and the other from the hydrogen atom. The H_2O MO is determined by considering properties of the binding atoms and the boundary constraints. The H_2 prolate spheroidal MO satisfies the boundary constraints as shown in the Nature of the Chemical Bond of Hydrogen-Type Molecules section; thus, each H-atom electron forms a H_2-type ellipsoidal MO with one of the initially unpaired O-atom electrons. The initial O electron configuration given in the Eight-Electron Atoms section is $1s^2 2s^2 2p^4$, and the orbital arrangement is given by Eqs. (10.154) and Eq. (13.55).

As shown in the case of OH in the Force Balance of OH section, the forces that determine the radius and the energy of the $O2p$ shell are unchanged with bond formation. Thus, the angular momentum of each electron of the $O2p$ is conserved with bond formation. The central paramagnetic force due to spin of each $O-H$ bond is provided by the spin-paring force of the H_2O MO that has the symmetry of an s orbital that superimposes with the $O2p$ orbitals such that the corresponding angular momenta are unchanged.

Each of the $O2p_z$ and $O2p_x$ electron combines with a $H1s$ electron to form a molecular orbital. The proton of the H atom is along the internuclear axis. Due to symmetry, the other O electrons are equivalent to point charges at the origin. (See Eqs. (19-

38) of Appendix IV.) Thus, the energies in the H_2O MO involve only each $O2p$ and each $H1s$ electron with the formation of each $O-H$ bond. The forces are determined by these energies.

As in the case of H_2, each of two $O-H$ -bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the O atom for distances shorter than the radius of the $2p$ shell. Otherwise, the electric field of the other $O2p$ electrons would be perturbed, and the $2p$ shell would not be stable. The corresponding increase in energy of O would not be offset by any energy decrease in the $O-H$ -bond MO based on the distance from the O nucleus to the $H1s$ electron compared to those of the $O2p$ electrons. Thus, the MO surface comprises a prolate spheroid at each H proton that is continuous with the $2p$ shell at the O atom. The sum of the energies of the prolate spheroids is matched to that of the $2p$ shell.

The orbital energy E for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic T and potential V energies. $E=T+V$ is constant, and the closed orbits are those for which $T<|V|$, and the open orbits are those for which $T\geq|V|$. It can be shown that the time average of the kinetic energy, $<T>$, for elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, $|<V>|$. $<T>=1/2|<V>|$ [11]. In the case of an atomic orbital (AO), $E=T+V$, and for all points on the AO, $|E|=T=1/2|V|$. As shown in the Hydrogen-type Molecular Ions section, each point or coordinate position on the continuous two-dimensional electron MO defines an infinitesimal mass-density element which moves along an orbit comprising an elliptic plane cross section of the spheroidal MO through the foci. The motion is such that eccentric angle, θ, changes at a constant rate at each point. That is $\theta=\omega t$ at time t where ω is a constant, and

$$r(t)=\mathbf{i}a\cos\omega t+\mathbf{j}b\sin\omega t \tag{13.161}$$

Consider the boundary condition that the MO of H_2O comprises a linear combination of an oxygen AO and two H_2-type ellipsoidal MOs, one for each $O-H$ -bond. The charge density of each H_2-type ellipsoidal MO given by Eqs. (11.44-11.45) and (13.3-13.4) maintains that the surface is an equipotential; however, the potential and kinetic energy of a point on the surface changes as it orbits the central field. The potential energy is a maximum and the kinetic energy is a minimum at the semimajor axis, and the reverse occurs at the semiminor

axis. Since the time average of the kinetic energy, $<T>$, for elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, by symmetry, the $<T>=1/2<|V|>$ condition holds for 1/2 of each H_2-type ellipsoidal MO having the H focus and ending at the plane defined by the semiminor axes. The O nucleus comprises the other focus of each OH-MO component of the H_2O MO. The $O2p$ AO obeys the energy relationship for all points. Thus, the linear combination of the H_2-type ellipsoidal MO with the $O2p$ AO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $O2p$ AO in order to match the energy relationships. Thus, the H_2O MO must comprise two $O-H$-bonds with each comprising 75% of a H_2-type ellipsoidal MO (1/2 +25%) and an oxygen AO:

$$[1\ O2p_z\ AO+0.75\ H_2\ MO]+[1\ O2p_y\ AO+0.75\ H_2\ MO]\rightarrow H_2O\ MO \qquad (13.162)$$

The force balance of the H_2O MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.162). The force constant k of a H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by Eq. (11.65):

$$k=\frac{2e^2}{4\pi\varepsilon_o} \qquad (13.163)$$

Since the each H_2-type ellipsoidal MO comprises 75% of the $O-H$-bond MO, the electron charge density in Eq. (13.163) is given by $-0.75e$. Thus, k' of the each H_2-type-ellipsoidal-MO component of the H_2O MO is

$$k'=\frac{(0.75)2e^2}{4\pi\varepsilon_o} \qquad (13.164)$$

L for the electron equals $\hbar$; thus, the distance from the origin of each $O-H$-bond MO to each focus c' is given by Eqs. (11.79) and (13.164):

$$c'=a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 1.5a}}=\sqrt{\frac{2aa_0}{3}} \qquad (13.165)$$

The internuclear distance from Eq. (13.165) is

$$2c'=2\sqrt{\frac{2aa_0}{3}} \qquad (13.166)$$

The length of the semiminor axis of the prolate spheroidal $O-H$ -bond MO $b=c$ given by Eq. (11.80) is

$$b=\sqrt{a^2-c'^2} \tag{13.167}$$

The eccentricity, e, is

$$e=\frac{c'}{a} \tag{13.168}$$

The solution of the semimajor axis a then allows for the solution of the other axes of the prolate spheroid and eccentricity of the $O-H$ -bond MO.

The general equation of the ellipsoidal MO having semiprincipal axes a, b, c given by

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{c^2}=1 \tag{13.169}$$

is also completely determined by the total energy E given by Eq. (11.18):

$$r=\frac{m\frac{L^2}{m^2}k^{-1}}{1+\left(1+2Em\frac{L^2}{m^2}k^{-2}\right)^{1/2}\cos\theta} \tag{13.170}$$

The energy of the oxygen $2p$ shell is the negative of the ionization energy of the oxygen atom given by Eqs. (10.163) and (13.66). Experimentally, the energy is [12]

$$E(2p\ shell)=-E(ionization;\ O)=-13.6181\ eV \tag{13.171}$$

Since each of the two prolate spheroidal $O-H$ -bond MOs comprises a H_2-type-ellipsoidal MO that transitions to the O AO, the energy E in Eq. (13.171) adds to that of the two corresponding H_2-type ellipsoidal MOs to give the total energy of the H_2O MO. From the energy equation and the relationship between the axes given by Eqs. (13.165-13.168), the dimensions of the H_2O MO are solved.

The energy components defined previously for the molecule, Eqs. (11.207-11.212), apply in the case of H_2O. Since the H_2O MO comprises two equivalent $O-H$ -bond MOs, each a linear combination of a H_2-type-ellipsoidal MO and an $O2p$ AO, the corresponding energy component of the H_2O MO is given by the linear superposition of the component energies. Thus, the energy scale factor is given as two times the force factor, the term in parentheses in Eq. (13.164). In addition to the equivalence and linearity principles, this factor also arises from the consideration of the nature of each bond and the linear combination that

forms the H_2O MO. Each $O-H$ -bond-energy component is the total for the two equivalent electrons with the exception that the total charge of the two electrons is normalized over the three basis set functions, two $O-H$ -bond MOs (OH -type ellipsoidal MOs given in the Energies of OH section) and one $O2p$ AO. Thus, the contribution of the $O-H$ -bond MOs to the H_2O MO energies are those given for $H_2(1/p)$ in the Energies of Hydrogen-Type Molecules multiplied by a factor of $3/2$ as in the case with H_3^+ (Eqs. (13.12), (13.15), 13.18-13.20)). In addition, the two sets of equivalent nuclear-point-charge pairs give rise to a factor of two times the proton-proton repulsion energy given by Eq. (11.208). Thus, the component energies of the H_2O MO are twice the corresponding energies of the OH MO given by Eqs. (13.67-13.73). The parameters a, b, and c' are given by Eqs. (13.165-13.167), respectively.

$$V_e = 2\left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left(\frac{3}{2}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (13.172)$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \quad (13.173)$$

$$T = 2\left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left(\frac{3}{2}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (13.174)$$

$$V_m = 2\left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \left(\frac{3}{2}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \quad (13.175)$$

$$E_T = V_e + T + V_m + V_p \quad (13.176)$$

$$E_T = -\frac{e^2}{4\pi\varepsilon_0\sqrt{a^2-b^2}}\left[\left(\frac{3}{2}-\frac{3}{4}\frac{a_0}{a}+\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right] \quad (13.177)$$

$$E_T = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \quad (13.178)$$

Since the each prolate spheroidal H_2 -type MO transitions to the O AO and the energy of the $O2p$ shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.171), the total energy $E_T(H_2O)$ of the H_2O MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the O AO and the two H_2 -type ellipsoidal MOs that forms the H_2O MO as given by Eq. (13.162):

$$E_T(H_2O) = E_T + E(2p\ shell)$$
$$= E_T - E(ionization;\ O)$$
$$= -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV \quad (13.179)$$

The two hydrogen atoms and the oxygen atom can achieve an energy minimum as a linear combination of two H_2-type ellipsoidal MOs each having the proton and the oxygen nucleus as the foci. Each $O-H$-bond MO comprises the same $O2p$ shell of constant energy given by Eq. (13.171). Thus, the energy of the H_2O MO is also given by the sum of that of the two H_2-type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant oxygen atom of the linear combination given by Eq. (13.171):

$$E_T(2H_2-O) = -2\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]-E(2p\ shell)$$
$$= 2(-31.63536831\ eV)-(-13.6181\ eV) \quad (13.180)$$
$$= -49.652637\ eV$$

$E_T(H_2O)$ given by Eq. (13.179) is set equal to two times the energy of the H_2-type ellipsoidal MO minus the energy of the $O2p$ shell given by Eq. (13.180):

$$E_T(H_2O) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV = -49.652637\ eV \quad (13.181)$$

From the energy relationship given by Eq. (13.181) and the relationship between the axes given by Eqs. (13.165-13.167), the dimensions of the H_2O MO can be solved.

Substitution of Eq. (13.165) into Eq. (13.181) gives

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e36.034537 \quad (13.182)$$

The most convenient way to solve Eq. (13.182) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.2641a_0 = 6.68933\ X\ 10^{-11}\ m \quad (13.183)$$

Substitution of Eq. (13.183) into Eq. (13.165) gives

$$c' = 0.918005a_0 = 4.85787\ X\ 10^{-11}\ m \quad (13.184)$$

The internuclear distance given by multiplying Eq. (13.184) by two is

$$2c' = 1.83601 a_0 = 9.71574\, X\ 10^{-11}\ m \tag{13.185}$$

The experimental bond distance is [23]

$$2c' = 9.70 \pm .005\, X\ 10^{-11}\ m \tag{13.186}$$

Substitution of Eqs. (13.177-13.176) into Eq. (13.167) gives

$$b = c = 0.869031 a_0 = 4.59871\, X\ 10^{-11}\ m \tag{13.187}$$

Substitution of Eqs. (13.177-13.176) into Eq. (13.168) gives

$$e = 0.726212 \tag{13.188}$$

The nucleus of the H atom and the nucleus of the O atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of each H_2-type ellipsoidal MO and the $O2p_y$ AO or $O2p_z$ AO can be determined from the polar equation of the ellipse (Eq. (11.10)):

$$r = r_0 \frac{1+e}{1+e\cos\theta'} \tag{13.189}$$

The radius of the $O2p$ shell given by Eq. (10.162) is $r_8 = a_0$, and the polar radial coordinate of the ellipse and the radius of the $O2p$ shell are equal at the point of intersection. Thus, Eq. (13.189) becomes

$$a_0 = (a-c')\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'} \tag{13.190}$$

such that the polar angle θ' is given by

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{a_0}-1\right)\right) \tag{13.191}$$

Substitution of Eqs. (13.177-13.176) into Eq. (13.191) gives

$$\theta' = 123.66° \tag{13.192}$$

Then, the angle θ_{O2pAO} the radial vector of the $O2p$ AO makes with the internuclear axis is

$$\theta_{O2pAO} = 180° - 123.66° = 56.33° \tag{13.193}$$

as shown in Figure 7. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the O radial vector obeys the following relationship:

$$a_0 \sin\theta_{O2pAO} = b \sin\theta_{H_2MO} \tag{13.194}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{a_0 \sin\theta_{O2pAO}}{b} = \sin^{-1}\frac{a_0 \sin 56.33°}{b} \tag{13.195}$$

with the use of Eq. (13.193). Substitution of Eq. (13.188) into Eq. (13.195) gives

$$\theta_{H_2MO} = 73.28° \tag{13.196}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.197}$$

Substitution of Eqs. (13.183) and (13.196) into Eq. (13.197) gives

$$d_{H_2MO} = 0.3637a_0 = 1.9244\,X\,10^{-11}\ m \tag{13.198}$$

The distance d_{O2pAO} along the internuclear axis from the origin of the O atom to the point of intersection of the orbitals is given by

$$d_{O2pAO} = c' - d_{H_2MO} \tag{13.199}$$

Substitution of Eqs. (13.184) and (13.198) into Eq. (13.199) gives

$$d_{O2pAO} = 0.5543a_0 = 2.93343\,X\,10^{-11}\ m \tag{13.200}$$

In addition to the intersection of the H_2-type MO with the $O2p$ shell, two adjoining ellipsoidal H_2-type MOs intersect at points of equipotential. The angle and distance parameters are given by Eqs. (13.595-13.600) for the limiting methane case wherein four adjoining intersecting H_2-type MOs have the possibility of forming a self-contained two-dimension equipotential surface of charge and current. Charge continuity can be obeyed for the H_2O MO if the current is continuous between the adjoining H_2-type MOs. However, in the limiting case of methane, the existence of a separate linear combination of the H_2-type MOs comprising four-spin paired electrons, not connected to the bonding carbon heteroatom requires that the electron be divisible. It is possible for an electron to form time-dependent singular points or nodes having no charge as shown by Eqs. (1.65a-1.65b), and two-dimensional charge distributions having Laplacian potentials and one-dimensional regions of zero charge are possible for macroscopic charge densities and currents as given in Haus and Melcher [24]. However, it is not possible for single electrons to have two dimensional discontinuities in charge based on internal forces and first principles discussed in Appendix

IV. Thus, at the points of intersection of the H_2-type MOs of methane, symmetry, electron indivisibility, current continuity, and conservation of energy and angular momentum require that the current between the points of mutual contact and the carbon atom be projected onto and flow along the radial vector to the surface of the $C2sp^3$ shell. This current designed the bisector current (BC) meets the $C2sp^3$ surface and does not travel to distances shorter than its radius. The methane result must also apply in the case of other bonds including that of the water molecule. Here, the H_2-type MOs intersect and the ellipsoidal current is projected onto the radial vector to the $O2p$ shell and does not travel to distances shorter than its radius as in the case of a single $O-H$ bond.

As shown in Eq. (13.162), in addition to the p-orbital charge-density modulation, the uniform charge-density in the p_z and p_y orbitals is increased by a factor of 0.25 and the H atoms are each decreased by a factor of 0.25. Using the orbital composition of H_2O (Eq. (13.162)), the radii of $O1s = 0.12739a_0$ (Eq. (10.51)), $O2s = 0.59020a_0$ (Eq. (10.62)), and $O2p = a_0$ (Eq. (10.162)) shells, and the parameters of the H_2O MO given by Eqs. (13.3-13.4), (13.183-13.185), (13.187-13.188), and (13.192-13.200), the charge-density of the H_2O MO comprising the linear combination of two $O-H$-bond MOs (OH-type ellipsoidal MOs given in the Energies of OH section) according to Eq. (13.162) is shown in Figure 9. Each $O-H$-bond MO comprises a H_2-type ellipsoidal MO and an $O2p$ AO having the dimensional diagram shown in Figure 8.

ENERGIES OF H_2O

The energies of H_2O given by the substitution of the semiprincipal axes (Eqs. (13.183-13.185) and (13.187)) into the energy equations (Eqs. (13.172-13.180)) are

$$V_e = \left(\frac{3}{2}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -81.8715\ eV \tag{13.201}$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 29.6421\ eV \tag{13.202}$$

$$T = \left(\frac{3}{2}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 32.3833\ eV \tag{13.203}$$

$$V_m = \left(\frac{3}{2}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.1917\ eV \quad (13.204)$$

$$E_T(H_2O) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-13.6181\ eV = -49.6558\ eV \quad (13.205)$$

where $E_T(H_2O)$ is given by Eq. (13.179) which is reiteratively matched to Eq. (13.180) within five-significant-figure round-off error.

VIBRATION OF H_2O

The vibrational energy levels of H_2O may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERM OF H_2O

The radiation reaction force in the case of the vibration of H_2O in the transition state corresponds to the Doppler energy, E_D, given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. As in the case of H_3^+, the water molecule is a linear combination of three orbitals. The water MO comprises two H_2-type ellipsoidal MOs and the O AO. Thus, the force factor of water in the determination of the Doppler frequency is equivalent to that of the H_3^+ ion given in Eqs. (13.18-13.20) and given by Eq. (13.164). From Eqs. (11.231-11.232) and (13.18-13.20), the central force terms between the electron density and the nuclei of each $O-H$ -bond MO with the radius of the orbit at the oxygen atom fixed at

$$r_8 = a_0 \quad (13.206)$$

according to Eq. (10.162) with the oscillation along the semiminor axis are

$$f(b) = -\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^2} \quad (13.207)$$

and

$$f'(b)=\left(\frac{3}{2}\right)\frac{2e^2}{4\pi\varepsilon_0 b^3} \tag{13.208}$$

Thus, using Eqs. (11.136) and (13.207-13.208), the angular frequency of this oscillation is

$$\omega=\sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}}=6.24996\,X\,10^{16}\ rad/s \tag{13.209}$$

The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K=\hbar\omega=\hbar 6.24996\,X\,10^{16}\ rad/s=41.138334\ eV \tag{13.210}$$

The three basis elements of water, H, H, and O, all have the same Coulombic energy as given by Eqs. (1.243) and (10.163), respectively, such that the Doppler energy involves the total energy of the H_2O MO. Thus, in Eq. (11.181), substitution of the total energy of H_2O, $E_T(H_2O)$, (Eqs. (13.179-13.180) and Eq. (13.181)) for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.210) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}=-49.652637\ eV\sqrt{\frac{2e(41.138334\ eV)}{m_e c^2}}=-0.630041\ eV \tag{13.211}$$

The total energy of H_2O is decreased by $\overline{E}_D$.

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. On average, the total energy of vibration is equally distributed between kinetic energy and potential energy [4]. Thus, the average kinetic energy of vibration corresponding to the Doppler energy of the electrons, $\overline{E}_{Kvib}$, is 1/2 of the vibrational energy of H_2O. The decrease in the energy of H_2O due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ and $\overline{E}_{Kvib}$. Using Eq. (13.211) and the experimental $H^{16}OH$ vibrational energy of $E_{vib}=3755.93\ cm^{-1}=0.465680\ eV$ [25] gives

$$\overline{E}'_{osc}=\overline{E}_D+\overline{E}_{Kvib}=\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.212}$$

$$\overline{E}'_{osc}=-0.630041\ eV+\frac{1}{2}(0.465680\ eV)=-0.397201\ eV \tag{13.213}$$

per bond. As in the case for $H_3^+(1/p)$ shown in the Doppler Energy Term of H_3^+-type Molecular Ions section, the reentrant orbit for the binding of a hydrogen atom to a hydroxyl radical causes the bonds to oscillate by increasing and decreasing in length along the two $O-H$ bonds at a relative phase angle of 180°. Since the vibration and reentrant oscillation is along two bonds for the asymmetrical stretch (v_3), $\overline{E}_{osc}$ for $H^{16}OH$, $\overline{E}_{osc}\left(H^{16}OH\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left(H^{16}OH\right) &= 2\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 2\left(-0.630041\ eV + \frac{1}{2}(0.465680\ eV)\right)\\ &= -0.794402\ eV\end{aligned} \tag{13.214}$$

To the extent that the MO dimensions are the same, the electron reentrant orbital energies, $\overline{E}_K$, are the same independent of the isotope of hydrogen, but the vibrational energies are related by Eq. (11.148). Thus, the differences in bond energies are essentially given by 1/2 the differences in vibrational energies per bond. Using Eq. (13.211), Eqs. (13.212-13.214), and the experimental $D^{16}OD$ vibrational energy of $E_{vib} = 2787.92\ cm^{-1} = 0.345661\ eV$ [25], the corresponding $\overline{E}_{osc}\left(D^{16}OD\right)$ is

$$\begin{aligned}\overline{E}_{osc}\left(D^{16}OD\right) &= 2\left(-0.630041\ eV + \frac{1}{2}(0.345661\ eV)\right)\\ &= -0.914421\ eV\end{aligned} \tag{13.215}$$

TOTAL AND BOND ENERGIES OF $H^{16}OH$ AND $D^{16}OD$

$E_{T+osc}\left(H_2{}^{16}O\right)$, the total energy of the $H^{16}OH$ including the Doppler term, is given by the sum of $E_T(H_2O)$ (Eq. (13.181)) and $\overline{E}_{osc}\left(H^{16}OH\right)$ given Eqs. (13.207-13.214):

$$\begin{aligned}E_{T+osc}\left(H_2{}^{16}O\right) &= V_e + T + V_m + V_p + E(O2p) + \overline{E}_{osc}\left(H^{16}OH\right)\\ &= E_T(H_2O) + \overline{E}_{osc}\left(H^{16}OH\right)\end{aligned} \tag{13.216}$$

$$E_{T+osc}\left(H_2{}^{16}O\right)=\left\{\begin{array}{l}\left(\frac{-e^2}{4\pi\varepsilon_0 c'}\left(\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right)-13.6181\ eV\right)\left(1+2\sqrt{\frac{2\hbar\sqrt{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}{m_e c^2}}\right)\\ +2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\}$$

$$=-49.652637\ eV-2\left(0.630041\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{13.217}$$

From Eqs. (13.214) and (13.216-13.217), the total energy of $H^{16}OH$ is

$$\begin{aligned}E_{T+osc}\left(H_2{}^{16}O\right)&=-49.652637\ eV+\overline{E}_{osc}\left(H^{16}OH\right)\\&=-49.652637\ eV-2\left(0.630041\ eV-\frac{1}{2}(0.465680\ eV)\right)\\&=-50.447039\ eV\end{aligned} \tag{13.218}$$

where the experimental vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left(D_2{}^{16}O\right)$, the total energy of $D^{16}OD$ including the Doppler term is given by the sum of $E_T\left(D_2O\right)=E_T\left(H_2O\right)$ (Eq. (13.181)) and $\overline{E}_{osc}\left(D^{16}OD\right)$ given by Eq. (13.215):

$$\begin{aligned}E_{T+osc}\left(D_2{}^{16}O\right)&=-49.652637\ eV+\overline{E}_{osc}\left(D^{16}OD\right)\\&=-49.652637\ eV-2\left(0.630041\ eV-\frac{1}{2}(0.345661\ eV)\right)\\&=-50.567058\ eV\end{aligned} \tag{13.219}$$

where the experimental vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. As in the case of the hydroxyl radical, the dissociation of the bond of the water molecule forms a free hydrogen atom and a hydroxyl radical, with one unpaired electron each. The lowering of the energy of the reactants due to the magnetic dipoles decreases the bond energy. Thus, the total energy of oxygen is reduced by the energy in the field of the two magnetic dipoles given by Eq. (13.152). The corresponding bond dissociation energy, E_D, is given by the sum of the total

energies of the corresponding hydroxyl radical and hydrogen atom minus the total energy of water, $E_{T+osc}\left(H^{16}OH\right)$, and $E(magnetic)$.

Thus, E_D of $H^{16}OH$ is given by:

$$E_D\left(H^{16}OH\right)=E(H)+E(^{16}OH)-E_{T+osc}\left(H^{16}OH\right)-E(magnetic) \quad (13.220)$$

where $E_T(^{16}OH)$ is given by the of the sum of the experimental energies of ^{16}O (Eq. (13.171)), H (Eq. (13.154)), and the negative of the bond energy of ^{16}OH (Eq. (13.157)):

$$E(^{16}OH)=-13.59844\ eV-13.6181\ eV-4.41174\ eV=-31.62828\ eV \quad (13.221)$$

From Eqs. (13.154), (13.218), and (13.220-13.221), $E_D\left(H^{16}OH\right)$ is

$$\begin{aligned}E_D(H^{16}OH)&=E(H)+E(^{16}OH)-\left(E(magnetic)+E_{T+osc}\left(H^{16}OH\right)\right)\\&=-13.59844\ eV-31.62828\ eV-\left(0.114411\ eV-50.447039\ eV\right)\\&=5.1059\ eV\end{aligned} \quad (13.222)$$

The experimental $H^{16}OH$ bond dissociation energy is [26]

$$E_D(H^{16}OH)=5.0991\ eV \quad (13.223)$$

Similarly, E_D of $D^{16}OD$ is given by:

$$E_D\left(D^{16}OH\right)=E(D)+E(^{16}OD)-\left(E(magnetic)+E_{T+osc}\left(D^{16}OD\right)\right) \quad (13.224)$$

where $E_T(^{16}OD)$ is given by the of the sum of the experimental energies of ^{16}O (Eq. (13.171)), D (Eq. (13.155)), and the negative of the bond energy of ^{16}OD (Eq. (13.159)):

$$E(^{16}OD)=-13.603\ eV-13.6181\ eV-4.454\ eV=-31.6721\ eV \quad (13.225)$$

From Eqs. (13.155), (13.220), and (13.224-13.225), $E_D\left(D^{16}OD\right)$ is

$$\begin{aligned}E_D(D^{16}OD)&=-13.603\ eV-31.6721\ eV-\left(0.114411\ eV-50.567058\ eV\right)\\&=5.178\ eV\end{aligned} \quad (13.226)$$

The experimental $D^{16}OD$ bond dissociation energy is [27]

$$E_D(D^{16}OD)=5.191\ eV \quad (13.227)$$

BOND ANGLE OF H_2O

The H_2O MO comprises a linear combination of two $O-H$ -bond MOs. Each $O-H$ -bond MO comprises the superposition of a H_2-type ellipsoidal MO and the $O2p_z$ AO or the

$O2p_y$ AO with a relative charge-density of 0.75 to 1.25; otherwise, the $O2p$ orbitals are the same as those of the oxygen atom. A bond is also possible between the two H atoms of the $O-H$ bonds. Such $H-H$ bonding would decrease the $O-H$ -bond strength since electron density would be shifted from the $O-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $O-H$ bonds is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal H atoms of the $O-H$ bonds is zero. Since the two H_2-type ellipsoidal MOs comprise 75% of the H electron density of H_2; the energies and the total energy E_T of the $H-H$ bond is given by Eqs. (13.67-13.73). From Eq. (11.79), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{13.228}$$

The internuclear distance from Eq. (13.228) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.229}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (13.167). Substitution of Eq. (13.228) into Eq. (13.73) gives

$$E_T = -\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right] \tag{13.230}$$

The radiation reaction force in the case of the vibration of $H-H$ in the transition state corresponds to the Doppler energy, E_D, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy E_T that includes the radiation reaction of the $H-H$ MO is given by the sum of E_T (Eq. (13.73)) and $\overline{E}_{osc}(H_2)$ given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy $E_T(H-H)$ of the $H-H$ MO including the Doppler term is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}(H-H) \tag{13.231}$$

$$E_T = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right]+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

$$=\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right] \tag{13.232}$$

$$+\frac{1}{2}\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o a^3}-\frac{e^2}{8\pi\varepsilon_o(a+c')^3}}{0.5m_p}}$$

To match the boundary condition that the total energy of the $H-H$ ellipsoidal MO is zero, $E_T(H-H)$ given by Eq. (13.232) is set equal to zero:

$$0=\left[\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right]\right. \tag{13.233}$$

$$\left.+\frac{1}{2}\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o a^3}-\frac{e^2}{8\pi\varepsilon_o(a+c')^3}}{0.5m_p}}\right]$$

From the energy relationship given by Eq. (13.233) and the relationship between the axes given by Eqs. (13.165-13.167), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (13.233) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 4.300a_0 = 2.275\ X\ 10^{-10}\ m \tag{13.234}$$

Substitution of Eq. (13.234) into Eq. (13.228) gives

$$c' = 1.466a_0 = 7.759\ X\ 10^{-11}\ m \tag{13.235}$$

The internuclear distance given by multiplying Eq. (13.235) by two is

$$2c' = 2.933a_0 = 1.552\ X\ 10^{-10}\ m \tag{13.236}$$

Substitution of Eqs. (13.234-13.235) into Eq. (13.167) gives

$$b = c = 4.042a_0 = 2.139\ X\ 10^{-10}\ m \tag{13.237}$$

Substitution of Eqs. (13.234-13.235) into Eq. (13.168) gives

$$e = 0.341 \tag{13.238}$$

Using, distance between the two H atoms when the total energy of the corresponding MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$A^2 + B^2 - 2AB\text{cosine}\theta = C^2 \tag{13.239}$$

With $A = B = 2c'_{O-H}$, the internuclear distance of each $O-H$ bond given by Eq. (13.185), and $C = 2c'_{H-H}$, the internuclear distance of the two H atoms, the bond angle between the $O-H$ bonds is given by

$$\left(2c'_{O-H}\right)^2 + \left(2c'_{O-H}\right)^2 - 2\left(2c'_{O-H}\right)^2 \text{cosine}\theta = \left(2c'_{H-H}\right)^2 \tag{13.240}$$

$$\theta = \cos^{-1}\left(\frac{2\left(2c'_{O-H}\right)^2 - \left(2c'_{H-H}\right)^2}{2\left(2c'_{O-H}\right)^2}\right) \tag{13.241}$$

Substitution of Eqs. (13.185) and (13.236) into Eq. (13.241) gives

$$\begin{aligned}\theta &= \cos^{-1}\left(\frac{2(1.836)^2 - (2.933)^2}{2(1.836)^2}\right)\\ &= \cos^{-1}(-0.2756)\\ &= 105.998^\circ\end{aligned} \tag{13.242}$$

The experimental internuclear distance of the two H atoms, $2c'_{H-H}$, is [23]

$$2c'_{H-H} = 1.55 \pm 0.01\ X\ 10^{-10}\ m \tag{13.243}$$

which matches Eq. (13.236) very well. The experimental angle between the $O-H$ bonds is [23]

$$\theta = 106^\circ \tag{13.244}$$

which matches the predicted angle given by Eq. (13.242).

The results of the determination of bond parameters of H_2O and D_2O are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

HYDROGEN NITRIDE (NH)

The ammonia molecule can be solved by first considering the solution of the hydrogen and dihydrogen nitride radicals. The former is formed by the reaction of a hydrogen atom and a nitrogen atom:

$$H + N \rightarrow NH \tag{13.245}$$

The hydrogen nitride radicals, NH and NH_2, and ammonia, NH_3, can be solved using the same principles as those used to solve OH and H_2O.

FORCE BALANCE OF NH

NH comprises two spin-paired electrons in a chemical bond between the nitrogen atom and the hydrogen atom such that two electrons on N remain unpaired. The NH radical molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal H_2 MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the H-atom electron forms a H_2-type ellipsoidal MO with one of the N-atom electrons. The N electron configuration given in the Seven-Electron Atoms section is $1s^2 2s^2 2p^3$, and the orbital arrangement is

$$\begin{array}{ccc} & 2\text{p state} & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} \\ 1 & 0 & -1 \end{array} \tag{13.246}$$

corresponding to the ground state ${}^4S^0_{3/2}$. The $N2p_x$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the H atom is along the internuclear axis. Due to symmetry, the other N electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the NH MO involve only the $N2p_x$ and $H1s$ electrons and the change in the magnetic energy of the $N2p_x$ electron with the other N electrons (Eq. (13.305)) with the formation of the NH MO. The forces are determined by these energies.

As in the case of H_2, the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into N atom for distances shorter than the radius of the $2p$ shell. Thus, the MO surface comprises a prolate spheroid at the H proton that is continuous with the $2p$ shell at the N atom whose nucleus serves as the other focus. The energy of the prolate spheroid is matched to that of the $N2p$ shell. As in the case with OH, the linear combination of the H_2-type ellipsoidal MO with the $N2p$ AO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $N2p$ atomic orbital (AO) in order to match potential, kinetic, and orbital energy relationships. Thus, the NH MO must comprise 75% of a H_2-type ellipsoidal MO and a nitrogen AO:

$$1\,N2p_x\,AO + 0.75\,H_2\,MO \rightarrow NH\,MO \tag{13.247}$$

The force balance of the NH MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.247) and the energy matching condition between the hydrogen and nitrogen components of the MO.

Similar to the OH case given by Eq. (13.59), the H_2-type ellipsoidal MO comprises 75% of the NH MO; so, the electron charge density in Eq. (11.65) is given by $-0.75e$. Based on the condition that the electron MO is an equipotential energy surface, Eq. (11.79) gives the ellipsoidal parameter c' in terms of the central force of the foci, the electron angular momentum, and the ellipsoidal parameter a. To meet the equipotential condition of the union of the H_2-type-ellipsoidal-MO and the N AO, the force constant used to determine the ellipsoidal parameter c' is normalized by the ratio of the ionization energy of N 14.53414 eV [6] and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). This normalizes the force to match that of the Coulombic force alone to met the force matching condition of the NH MO under the influence of the proton and the N nucleus. Thus, k' of Eq. (11.79) to determine c' is

$$k' = \frac{(0.75)2e^2}{4\pi\varepsilon_0 \frac{14.53414}{13.605804}} = (0.936127)\frac{(0.75)2e^2}{4\pi\varepsilon_0} \tag{13.248}$$

L for the electron equals $\hbar$; thus, the distance from the origin of the NH MO to each focus c' is given by Eqs. (11.79) and (13.248):

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 1.5a(0.936127)}} = \sqrt{\frac{2aa_0}{3(0.936127)}} = \sqrt{0.712154aa_0} \tag{13.249}$$

The internuclear distance from Eq. (13.249) is

$$2c' = 2\sqrt{0.712154aa_0} \tag{13.250}$$

The length of the semiminor axis of the prolate spheroidal NH MO $b = c$ is given by Eqs. (11.80) and (13.62). The eccentricity, e, is given by Eq. (13.63). Then, the solution of the semimajor axis a allows for the solution of the other axes of the prolate spheroidal and eccentricity of the NH MO.

The energy of the nitrogen $2p$ shell is the negative of the ionization energy of the nitrogen atom given by Eq. (10.143). Experimentally, the energy is [6]

$$E(2p\ shell) = -E(ionization;\ N) = -14.53414\ eV \tag{13.251}$$

Since the prolate spheroidal MO transitions to the N AO, the energy E in Eq. (13.251) adds to that of the H_2-type ellipsoidal MO to give the total energy of the NH MO. From the energy equation and the relationship between the axes given by Eqs. (13.249-13.250) and (13.62-13.63), the dimensions of the NH MO are solved.

The energy components of V_e, V_p, T, V_m, and E_T are the same as those of OH given by Eqs. (13.67-13.73). Similarly to OH, the total energy $E_T(NH)$ of the NH MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the N AO and the H_2-type ellipsoidal MO that forms the NH MO as given by Eq. (13.247):

$$\begin{aligned} E_T(NH) &= E_T + E(2p\ shell) \\ &= E_T - E(ionization;\ N) \\ &= -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV \end{aligned} \tag{13.252}$$

To match the boundary condition that the total energy of the entire the H_2-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_T(NH)$ given by Eq. (13.252) is set equal to Eq. (13.75):

$$E_T(NH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV = -31.63536831\ eV \tag{13.253}$$

From the energy relationship given by Eq. (13.252) and the relationship between the axes given by Eqs. (13.249-13.250) and (13.62-13.63), the dimensions of the NH MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.253) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{0.712154aa_0}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{0.712154aa_0}}{a-\sqrt{0.712154aa_0}}-1\right] = e17.10123 \tag{13.254}$$

The most convenient way to solve Eq. (13.254) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.36275a_0 = 7.21136\,X\,10^{-11}\ m \tag{13.255}$$

Substitution of Eq. (13.255) into Eq. (13.249) gives

$$c' = 0.98513a_0 = 5.21310\,X\,10^{-11}\ m \tag{13.256}$$

The internuclear distance given by multiplying Eq. (13.256) by two is

$$2c' = 1.97027a_0 = 1.04262\,X\,10^{-10}\ m \tag{13.257}$$

The experimental bond distance is [28]

$$2c' = 1.0362\,X\,10^{-10}\ m \tag{13.258}$$

Substitution of Eqs. (13.255-13.256) into Eq. (13.62) gives

$$b = c = 0.94159a_0 = 4.98270\,X\,10^{-11}\ m \tag{13.259}$$

Substitution of Eqs. (13.255-13.256) into Eq. (13.63) gives

$$e = 0.72290 \tag{13.260}$$

The nucleus of the H atom and the nucleus of the N atom comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $N2p_x$ AO are given by Eqs. (13.84-13.95). The polar intersection angle θ' is given by

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{r_n}-1\right)\right) \tag{13.261}$$

where $r_n = r_7 = 0.93084a_0$ is the radius of the N atom. Substitution of Eqs. (13.255-13.256) into Eq. (13.86) gives

$$\theta' = 114.61° \tag{13.262}$$

Then, the angle θ_{N2p_xAO} the radial vector of the $N2p_x$ AO makes with the internuclear axis is

$$\theta_{N2p_xAO} = 180° - 114.61° = 65.39° \tag{13.263}$$

as shown in Figure 10.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the N radial vector obeys the following relationship:

$$r_7 \sin\theta_{N2p_xAO} = 0.93084a_0 \sin\theta_{N2p_xAO} = b\sin\theta_{H_2MO} \tag{13.264}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.93084a_0 \sin\theta_{N2p_xAO}}{b} = \sin^{-1}\frac{0.93084a_0 \sin 65.39°}{b} \tag{13.265}$$

with the use of Eq. (13.263). Substitution of Eq. (13.259) into Eq. (13.265) gives

$$\theta_{H_2MO} = 64.00° \tag{13.266}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.267}$$

Substitution of Eqs. (13.255) and (13.266) into Eq. (13.267) gives

$$d_{H_2MO} = 0.59747a_0 = 3.16166\,X\,10^{-11}\ m \tag{13.268}$$

The distance d_{N2pAO} along the internuclear axis from the origin of the N atom to the point of intersection of the orbitals is given by

$$d_{N2pAO} = c' - d_{H_2MO} \tag{13.269}$$

Substitution of Eqs. (13.79) and (13.93) into Eq. (13.94) gives

$$d_{N2pAO} = 0.38767a_0 = 2.05144\,X\,10^{-11}\ m \tag{13.270}$$

As shown in Eq. (13.247), in addition to the p-orbital charge-density modulation, the uniform charge-density in the p_x orbital is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25. The internuclear axis of the $N-H$ bond is perpendicular to the bonding p_x orbital. Using the orbital composition of NH (Eq. (13.27)), the radii of $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), and $N2p = 0.93084a_0$ (Eq. (10.142)) shells, and the parameters of the NH MO given by Eqs. (13.3-13.4) and (13.255-13.270), the dimensional diagram and charge-density of the NH MO comprising the linear combination of the H_2-type ellipsoidal MO and the N AO according to Eq. (13.247) are shown in Figures 10 and 11, respectively.

ENERGIES OF NH

The energies of NH given by the substitution of the semiprincipal axes (Eqs. (13.255-13.256) and (13.259)) into the energy equations (Eqs. (13.67-13.73)) are

$$V_e = \left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -37.85748\ eV \tag{13.271}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 13.81113\ eV \tag{13.272}$$

$$T = \left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 13.89011\ eV \tag{13.273}$$

$$V_m = \left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -6.94505\ eV \tag{13.274}$$

$$E_T(NH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV = -31.63544\ eV \tag{13.275}$$

where $E_T(NH)$ is given by Eq. (13.253) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

VIBRATION AND ROTATION OF NH

The vibrational energy of NH may be solved in the same manner as that of OH. From Eqs. (13.102-13.106) with the substitution of the NH parameters, the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0 b^3}-\frac{e^2}{8\pi\varepsilon_0(2c')^3}}{\mu}} = \sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_0(0.94159a_0)^3}-\frac{e^2}{8\pi\varepsilon_0(1.97027a_0)^3}}{\frac{14}{15}m_p}} = 6.18700\ X\ 10^{14}\ rad/s \tag{13.276}$$

where b is given by Eq. (13.259), $2c'$ is given by Eq. (13.257), and the reduced mass of ^{14}NH is given by:

$$\mu_{^{14}NH} = \frac{m_1 m_2}{m_1+m_2} = \frac{(1)(14)}{1+14}m_p \tag{13.277}$$

where m_p is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for ^{14}NH given by Eqs. (11.136), (11.148), and (13.276) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{597.59\ Nm^{-1}}{\mu}} = 6.18700\ X\ 10^{14}\ radians/s \tag{13.278}$$

where the reduced nuclear mass of ^{14}NH is given by Eq.(13.277) and the spring constant, $k(0)$, given by Eqs. (11.136) and (13.276) is

$$k(0) = 597.59\ Nm^{-1} \tag{13.279}$$

The ^{14}NH transition-state vibrational energy, $E_{vib}(0)$, given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \hbar\omega = \hbar 6.18700\,X\,10^{14}\ rad/s = 0.407239\ eV = 3284.58\ cm^{-1} \tag{13.280}$$

ω_e, from the experimental curve fit of the vibrational energies of ^{14}NH is [28]

$$\omega_e = 3282.3\ cm^{-1} \tag{13.281}$$

Using Eqs. (13.112-13.118) with $E_{vib}(0)$ given by Eq. (13.280) and D_0 given by Eq. (13.311), the ^{14}NH $\upsilon = 1 \rightarrow \upsilon = 0$ vibrational energy, $E_{vib}(1)$ is

$$E_{vib}(1) = 0.38581\ eV \qquad \left(3111.84\ cm^{-1}\right) \tag{13.282}$$

The experimental vibrational energy of ^{14}NH using ω_e and $\omega_e x_e$ [28] according to K&P [15] is

$$E_{vib}(1) = 0.38752\ eV \qquad \left(3125.5\ cm^{-1}\right) \tag{13.283}$$

Using Eq. (13.113) with $E_{vib}(1)$ given by Eq. (13.282) and D_0 given by Eq. (13.311), the anharmonic perturbation term, $\omega_0 x_0$, of ^{14}NH is

$$\omega_0 x_0 = 86.37\ cm^{-1} \tag{13.284}$$

The experimental anharmonic perturbation term, $\omega_0 x_0$, of ^{14}NH [28] is

$$\omega_0 x_0 = 78.4\ cm^{-1} \tag{13.285}$$

The vibrational energies of successive states are given by Eqs. (13.280), (13.112), and (13.284).

Using b given by Eq. (13.259), $2c'$ given by Eq. (13.257), D_0 given by Eq. (13.314), and the reduced nuclear mass of ^{14}ND given by

$$\mu_{^{14}ND} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(14)}{2+14} m_p \tag{13.286}$$

where m_p is the proton mass, the corresponding parameters for deuterium nitride ^{14}ND (Eqs. (13.102-13.121)) are

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{597.59\ Nm^{-1}}{\mu}} = 4.51835\,X\,10^{14}\ radians/s \tag{13.287}$$

$$k(0) = 579.59\ Nm^{-1} \tag{13.288}$$

$$E_{vib}(0) = \hbar\omega = \hbar 4.51835\ X\ 10^{14}\ rad/s = 0.29741\ eV = 2398.72\ cm^{-1} \quad (13.289)$$

$$E_{vib}(1) = 0.28710\ eV \qquad \left(2305.35\ cm^{-1}\right) \quad (13.290)$$

$$\omega_0 x_0 = 47.40\ cm^{-1} \quad (13.291)$$

ω_e, from the experimental curve fit of the vibrational energies of ^{14}ND is [28]

$$\omega_e = 2398\ cm^{-1} \quad (13.292)$$

The experimental vibrational energy of ^{14}ND using ω_e and $\omega_e x_e$ [28] according to K&P [15] is

$$E_{vib}(1) = 0.2869\ eV \qquad \left(2314\ cm^{-1}\right) \quad (13.293)$$

and the experimental anharmonic perturbation term, $\omega_0 x_0$, of ^{14}ND [28] is

$$\omega_0 x_0 = 42\ cm^{-1} \quad (13.294)$$

which match the predictions given by Eqs. (13.289), (13.290) and (13.291), respectively.

Using Eqs. (13.133-13.134) and the internuclear distance, $r = 2c'$, and reduced mass of ^{14}NH given by Eqs. (13.257) and (13.277), respectively, the corresponding B_e is

$$B_e = 16.495\ cm^{-1} \quad (13.295)$$

The experimental B_e rotational parameter of ^{14}NH is [28]

$$B_e = 16.6993\ cm^{-1} \quad (13.296)$$

Using the internuclear distance, $r = 2c'$, and reduced mass of ^{14}ND given by Eqs. (13.257) and (13.286), respectively, the corresponding B_e is

$$B_e = 8.797\ cm^{-1} \quad (13.297)$$

The experimental B_e rotational parameter of ^{14}ND is [28]

$$B_e = 8.7913\ cm^{-1} \quad (13.298)$$

THE DOPPLER ENERGY TERMS OF ^{14}NH AND ^{14}ND

The equations of the radiation reaction force of hydrogen and deuterium nitride are the same as those of the corresponding hydroxyl radicals with the substitution of the hydrogen and deuterium nitride parameters. Using Eqs. (11.136) and (13.140-13.141), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 3.91850\,X\,10^{16}\ rad/s \tag{13.299}$$

where b is given by Eq. (13.259). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 3.91850\,X\,10^{16}\ rad/s = 25.79224\ eV \tag{13.300}$$

In Eq. (11.181), substitution of the total energy of NH, $E_T(NH)$, (Eq. (13.253)) for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.300) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(25.79224\ eV)}{m_e c^2}} = -0.31785\ eV \tag{13.301}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of NH due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.301) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of NH. Using the experimental ^{14}NH ω_e of $3282.3\ cm^{-1}$ $(0.40696\ eV)$ [28] $\overline{E}_{osc}(^{14}NH)$ is

$$\overline{E}_{osc}(^{14}NH) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.302}$$

$$\overline{E}_{osc}(^{14}NH) = -0.31785\ eV + \frac{1}{2}(0.40696\ eV) = -0.11437\ eV \tag{13.303}$$

Using Eqs. (13.301) and the experimental ^{14}ND ω_e of $2398\ cm^{-1}$ $(0.29732\ eV)$ [28] $\overline{E}_{osc}(^{14}ND)$ is

$$\overline{E}_{osc}(^{14}ND) = -0.31785\ eV + \frac{1}{2}(0.29732\ eV) = -0.16919\ eV \tag{13.304}$$

TOTAL AND BOND ENERGIES OF ^{14}NH AND ^{14}ND

$E_{T+osc}(NH)$, the total energy of the ^{14}NH radical including the Doppler term, is given by the sum of $E_T(NH)$ (Eq. (13.253)) and $\overline{E}_{osc}(^{14}NH)$ given by Eq. (13.303):

$$E_{T+osc}(NH) = V_e + T + V_m + V_p + E(2p\ shell) + \bar{E}_{osc}\left({}^{14}NH\right) = E_T(NH) + \bar{E}_{osc}\left({}^{14}NH\right) \tag{13.305}$$

$$E_{T+osc}(NH) = \left\{\frac{-e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 14.53414\ eV\right\}\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}m_e}}{m_e c^2}}\right] + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

$$= -31.63537\ eV - 0.31785\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.306}$$

From Eqs. (13.302-13.303) and (13.305-13.306), the total energy of ${}^{14}NH$ is

$$E_{T+osc}(NH) = -31.63537\ eV + \bar{E}_{osc}\left({}^{14}NH\right) = -31.63537\ eV - 0.31785\ eV + \frac{1}{2}(0.40696\ eV) = -31.74974\ eV \tag{13.307}$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}(ND)$, the total energy of ${}^{14}ND$ including the Doppler term, is given by the sum of $E_T(ND) = E_T(NH)$ (Eq. (13.253)) and $\bar{E}_{osc}\left({}^{14}ND\right)$ given by Eq. (13.304):

$$E_{T+osc}(ND) = -31.63537\ eV + \bar{E}_{osc}\left({}^{14}ND\right) = -31.63537\ eV - 0.31785\ eV + \frac{1}{2}(0.29732\ eV) = -31.80456\ eV \tag{13.308}$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. The dissociation of the bond of the hydrogen nitride forms a free hydrogen atom with one unpaired electron and a nitrogen atom with three unpaired electrons as shown in Eq. (13.246). The p_x and p_y fields cancel and the magnetic energy (Eq. (7.46) with $r_7 = 0.93084a_0$ is subtracted due to the one component of E_{mag} given by Eq. (10.137):

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(0.93084a_0\right)^3} = \frac{8\pi\mu_o\mu_B^2}{\left(0.93084a_0\right)^3} = 0.14185\ eV \tag{13.309}$$

The corresponding bond dissociation energy, E_D, is given by the sum of the total energies of the nitrogen atom and the corresponding hydrogen atom minus the sum of $E_{T+osc}(NH)$ and $E(magnetic)$:

$$E_D = E(^{14}N) + E(H) - E_{T+osc}(NH) - E(magnetic) \tag{13.310}$$

$E(^{14}N)$ is given by Eq. (13.251), $E_D(H)$ is given by Eq. (13.154), and $E_D(D)$ is given by Eq. (13.155). The ^{14}NH bond dissociation energy, $E_D(^{14}NH)$, is given by Eqs. (13.154), (13.251), (13.307), and (13.309-13.310):

$$\begin{aligned} E_D(^{14}NH) &= -(14.53414\ eV + 13.59844\ eV) - (E(magnetic) + E_{T+osc}(NH)) \\ &= -28.13258\ eV - (0.14185 - 31.74974\ eV) \\ &= 3.47530\ eV \end{aligned} \tag{13.311}$$

The experimental ^{14}NH bond dissociation energy from Ref. [29] and Ref. [30] is

$$E_D(^{14}NH) = 3.42\ eV \tag{13.312}$$

$$E_D(^{14}NH) \le 3.47\ eV \tag{13.313}$$

The ^{14}ND bond dissociation energy, $E_D(^{14}ND)$, is given by Eqs. (13.155), (13.251), (13.308), and (13.309-13.310):

$$\begin{aligned} E_D(^{14}ND) &= -(14.53414\ eV + 13.603\ eV) - (E(magnetic) + E_{T+osc}(ND)) \\ &= -28.13714\ eV - (0.14185 - 31.80456\ eV) \\ &= 3.5256\ eV \end{aligned} \tag{13.314}$$

The experimental ^{14}ND bond dissociation energy from Ref. [31] and Ref. [30] is

$$E_{D_{298}}(^{14}ND) \le 339\ kJ/mol = 3.513\ eV \tag{13.315}$$

$$E_D(^{14}ND) \le 3.54\ eV \tag{13.316}$$

The results of the determination of bond parameters of NH and ND are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

DIHYDROGEN NITRIDE (NH_2)

The dihydrogen nitride radical NH_2 is formed by the reaction of a hydrogen atom with a hydrogen nitride radical:

$$NH + H \rightarrow NH_2 \tag{13.317}$$

NH_2 can be solved using the same principles as those used to solve H_2O. Two diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with two nitrogen atomic orbitals (AOs) to form the MO of NH_2. The solution is very similar to that of NH except that there are two NH bonds in NH_2.

FORCE BALANCE OF NH_2

NH_2 comprises two chemical bonds between nitrogen and hydrogen. Each $N-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the nitrogen atom and the other from the hydrogen atom. Each H-atom electron forms a H_2-type ellipsoidal MO with one of the initially unpaired N-atom electrons, $2p_x$ or $2p_y$, such that the proton and the N nucleus serve as the foci. The initial N electron configuration given in the Seven-Electron Atoms section is $1s^2 2s^2 2p^3$, and the orbital arrangement is given by Eqs. (10.134) and (13.246). The radius and the energy of the $N2p$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $N-H$ bond is provided by the spin-pairing force of the NH_2 MO that has the symmetry of an s orbital that superimposes with the $N2p$ orbitals such that the corresponding angular momenta are unchanged.

As in the case of H_2, each of two $N-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into N atom for distances shorter than the radius of the $2p$ shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at each H proton that is continuous with the $2p$ shell at the N atom. The energies in the NH_2 MO involve only each $N2p$ and each $H1s$ electron with the formation of each $N-H$ bond. The sum of the energies of the prolate spheroids is matched to that of the $2p$ shell. The forces are determined by these energies. As in the case of NH, the linear combination of each H_2-type ellipsoidal MO with each $N2p$ AO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $N2p$ AO in order to match potential, kinetic, and orbital energy relationships. Thus, the NH_2 MO must comprise two

$N-H$ bonds with each comprising 75% of a H_2-type ellipsoidal MO (1/2 +25%) and a nitrogen AO:

$$[1\,N2p_x\,AO+0.75\,H_2\,MO]+[1\,N2p_y\,AO+0.75\,H_2\,MO]\rightarrow NH_2\,MO \qquad (13.318)$$

The force constant k' of the each H_2-type-ellipsoidal-MO component of the NH_2 MO is given by Eq. (13.248). The distance from the origin of each $N-H$-bond MO to each focus c' is given by Eq. (13.249). The internuclear distance is given by Eq. (13.250). The length of the semiminor axis of the prolate spheroidal $N-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $N-H$-bond MO. Since each of the two prolate spheroidal $N-H$-bond MOs comprises a H_2-type-ellipsoidal MO that transitions to the N AO, the energy E in Eq. (13.251) adds to that of the two corresponding H_2-type ellipsoidal MOs to give the total energy of the NH_2 MO. From the energy equation and the relationship between the axes, the dimensions of the NH_2 MO are solved.

The energy components of V_e, V_p, T, V_m, and E_T are twice those of OH and NH given by Eqs. (13.67-13.73) and equal to those of H_2O given by Eqs. (13.172-13.178). Similarly to H_2O, since the each prolate spheroidal H_2-type MO transitions to the N AO and the energy of the $N2p$ shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.251), the total energy $E_T(NH_2)$ of the NH_2 MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the N AO and the two H_2-type ellipsoidal MOs that forms the NH_2 MO as given by Eq. (13.318):

$$\begin{aligned} E_T(NH_2) &= E_T + E(2p\ shell) \\ &= E_T - E(ionization;\ N) \\ &= -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV \end{aligned} \qquad (13.319)$$

The two hydrogen atoms and the nitrogen atom can achieve an energy minimum as a linear combination of two H_2-type ellipsoidal MOs each having the proton and the nitrogen nucleus as the foci. Each $N-H$-bond MO comprises the same $N2p$ shell of constant

energy given by Eq. (13.251). Thus, the energy of the NH_2 MO is also given by the sum of that of the two H_2-type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant nitrogen atom of the linear combination given by Eq. (13.251):

$$\begin{aligned} E_T(2H_2 - N) &= -2\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2}\right] - E(2p\ shell) \\ &= 2(-31.63536831\ eV) - (-14.53414\ eV) \\ &= -48.73660\ eV \end{aligned} \tag{13.320}$$

$E_T(NH_2)$ given by Eq. (13.319) is set equal to two times the energy of the H_2-type ellipsoidal MO minus the energy of the $N2p$ shell given by Eq. (13.320):

$$E_T(NH_2) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 14.53414\ eV = -48.73660\ eV \tag{13.321}$$

From the energy relationship given by Eq. (13.321) and the relationship between the axes given by Eqs. (13.248-13.250) and (13.62-13.63), the dimensions of the NH_2 MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.321) gives

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{0.712154aa_0}}\left[\left(\frac{3}{2} - \frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{0.712154aa_0}}{a-\sqrt{0.712154aa_0}} - 1\right] = e34.20246 \tag{13.322}$$

The most convenient way to solve Eq. (13.322) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.36276a_0 = 7.21141\ X\ 10^{-11}\ m \tag{13.323}$$

Substitution of Eq. (13.323) into Eq. (13.249) gives

$$c' = 0.98514a_0 = 5.21312\ X\ 10^{-11}\ m \tag{13.324}$$

The internuclear distance given by multiplying Eq. (13.324) by two is

$$2c' = 1.97027a_0 = 1.04262\ X\ 10^{-10}\ m \tag{13.325}$$

The experimental bond distance is [32]

$$2c' = 1.024\ X\ 10^{-10}\ m \tag{13.326}$$

Substitution of Eqs. (13.323-13.324) into Eq. (13.62) gives

$$b = c = 0.94160a_0 = 4.98276\ X\ 10^{-11}\ m \tag{13.327}$$

Substitution of Eqs. (13.323-13.324) into Eq. (13.63) gives

$$e = 0.72290 \tag{13.328}$$

The nucleus of the H atom and the nucleus of the N atom comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of each H_2-type ellipsoidal MO and the $N2p_x$ AO or $N2p_y$ AO are given by Eqs. (13.84-13.95) and (13.261-13.270). Using Eqs. (13.323-13.325) and (13.327-13.328), the polar intersection angle θ' given by Eq. (13.261) with $r_n = r_7 = 0.93084a_0$ is

$$\theta' = 114.61° \tag{13.329}$$

Then, the angle θ_{N2pAO} the radial vector of the $N2p_x$ AO or $N2p_y$ AO makes with the internuclear axis is

$$\theta_{N2pAO} = 180° - 114.61° = 65.39° \tag{13.330}$$

as shown in Figure 10. The angle θ_{H_2MO} between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the N radial vector given by Eqs. (13.264-13.265), (13.327), and (13.330) is

$$\theta_{H_2MO} = 64.00° \tag{13.331}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.267), (13.323), and (13.331) is

$$d_{H_2MO} = 0.59748a_0 = 3.16175\,X\,10^{-11}\ m \tag{13.332}$$

The distance d_{N2pAO} along the internuclear axis from the origin of the N atom to the point of intersection of the orbitals given by Eqs. (13.269), (13.324), and (13.332) is

$$d_{N2pAO} = 0.38765a_0 = 2.05137\,X\,10^{-11}\ m \tag{13.333}$$

As shown in Eq. (13.318), in addition to the p-orbital charge-density modulation, the uniform charge-density in the p_x and p_y orbitals is increased by a factor of 0.25 and the H atoms are each decreased by a factor of 0.25. Using the orbital composition of NH_2 (Eq. (13.318)), the radii of $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), and $N2p = 0.93084a_0$ (Eq. (10.142)) shells, and the parameters of the NH_2 MO given by Eqs. (13.3-13.4) and (13.323-13.333), the charge-density of the NH_2 MO comprising the linear combination of two $N-H$-bond MOs (NH-type ellipsoidal MOs given in the Energies of NH section) according to Eq. (13.318) is shown in Figure 12. Each $N-H$-bond MO

comprises a H_2-type ellipsoidal MO and an $N2p$ AO having the dimensional diagram shown in Figure 10.

ENERGIES OF NH_2

The energies of NH_2 given by the substitution of the semiprincipal axes ((Eqs. (13.323-13.325) and (13.327)) into the energy equations (Eqs. (13.172-13.176)) are

$$V_e = \left(\frac{3}{2}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -75.71422\ eV \tag{13.334}$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 27.62216\ eV \tag{13.335}$$

$$T = \left(\frac{3}{2}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 27.77974\ eV \tag{13.336}$$

$$V_m = \left(\frac{3}{2}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -13.88987\ eV \tag{13.337}$$

$$E_T(NH_2) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV = -48.73633\ eV \tag{13.338}$$

where $E_T(NH_2)$ is given by Eq. (13.319) which is reiteratively matched to Eq. (13.320) within five-significant-figure round-off error.

VIBRATION OF NH_2

The vibrational energy levels of NH_2 may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERM OF NH_2

The radiation reaction force in the case of the vibration of NH_2 in the transition state corresponds to the Doppler energy, E_D, given by Eq. (11.181) and Eqs. (13.22) and (13.144)

that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. The equations of the radiation reaction force of dihydrogen and dideuterium nitride are the same as those of the corresponding water molecules with the substitution of the dihydrogen and dideuterium nitride parameters. Using Eqs. (11.136) and (13.207-13.209), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 5.54150\,X\,10^{16}\ rad/s \tag{13.339}$$

where b is given by Eq. (13.327). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 5.54150\,X\,10^{16}\ rad/s = 36.47512\ eV \tag{13.340}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.340) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(36.47512\ eV)}{m_e c^2}} = -0.37798\ eV \tag{13.341}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of NH_2 due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.341) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of NH_2. Using the experimental $^{14}NH_2$ vibrational energy of $E_{vib} = 3301.110\ cm^{-1} = 0.40929\ eV$ [33] gives

$$\overline{E}'_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.342}$$

$$\overline{E}'_{osc} = -0.37798\ eV + \frac{1}{2}(0.40929\ eV) = -0.17334\ eV \tag{13.343}$$

per bond. As in the case for H_2O, the reentrant orbit for the binding of a hydrogen atom to a NH radical causes the bonds to oscillate by increasing and decreasing in length along the

two $N-H$ bonds at a relative phase angle of 180°. Since the vibration and reentrant oscillation is along two bonds for the asymmetrical stretch (v_3), $\overline{E}_{osc}$ for $^{14}NH_2$, $\overline{E}_{osc}\left(^{14}NH_2\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left(^{14}NH_2\right) &= 2\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 2\left(-0.37798\ eV + \frac{1}{2}(0.40929\ eV)\right)\\ &= -0.34668\ eV\end{aligned} \tag{13.344}$$

Using Eq. (13.341), Eqs. (13.342-13.344), and the $^{14}ND_2$ vibrational energy of $E_{vib} = 2410.79\ cm^{-1} = 0.29890\ eV$, calculated from the experimental $^{14}NH_2$ vibrational energy using Eq. (11.148), the corresponding $\overline{E}_{osc}\left(^{14}ND_2\right)$ is

$$\begin{aligned}\overline{E}_{osc}\left(^{14}ND_2\right) &= 2\left(-0.37798\ eV + \frac{1}{2}(0.29890\ eV)\right)\\ &= -0.45707\ eV\end{aligned} \tag{13.345}$$

TOTAL AND BOND ENERGIES OF $^{14}NH_2$ AND $^{14}ND_2$

$E_{T+osc}\left(^{14}NH_2\right)$, the total energy of the $^{14}NH_2$ including the Doppler term, is given by the sum of $E_T\left(NH_2\right)$ (Eq. (13.321)) and $\overline{E}_{osc}\left(^{14}NH_2\right)$ given Eqs. (13.339-13.344):

$$\begin{aligned}E_{T+osc}\left(^{14}NH_2\right) &= V_e + T + V_m + V_p + E(N2p) + \overline{E}_{osc}\left(^{14}NH_2\right)\\ &= E_T\left(NH_2\right) + \overline{E}_{osc}\left(^{14}NH_2\right)\end{aligned} \tag{13.346}$$

$$\begin{aligned}E_{T+osc}\left(^{14}NH_2\right) &= \left\{\left(\frac{-e^2}{4\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV\right)\right.\\ &\left.-2\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}{m_e c^2}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\}\\ &= -48.73660\ eV - 2\left(0.37798\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{13.347}$$

From Eqs. (13.344) and (13.346-13.347), the total energy of $^{14}NH_2$ is

$$E_{T+osc}\left(^{14}NH_2\right) = -48.73660\ eV + \bar{E}_{osc}\left(^{14}NH_2\right)$$
$$= -48.73660\ eV - 2\left(0.37798\ eV - \frac{1}{2}(0.40929\ eV)\right) \quad (13.348)$$
$$= -49.08328\ eV$$

where the experimental $^{14}NH_2$ vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left(^{14}ND_2\right)$, the total energy of $^{14}ND_2$ including the Doppler term is given by the sum of $E_T(ND_2) = E_T(NH_2)$ (Eq. (13.321)) and $\bar{E}_{osc}\left(^{14}ND_2\right)$ given by Eq. (13.345):

$$E_{T+osc}\left(^{14}ND_2\right) = -48.73660\ eV + \bar{E}_{osc}\left(^{14}ND_2\right)$$
$$= -48.73660\ eV - 2\left(0.37798\ eV - \frac{1}{2}(0.29890\ eV)\right) \quad (13.349)$$
$$= -49.19366\ eV$$

where the experimental $^{14}NH_2$ vibrational energy corrected for the reduced mass difference of hydrogen and deuterium was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. The corresponding bond dissociation energy, E_D, is given by the sum of the total energies of the corresponding hydrogen nitride radical and hydrogen atom minus the total energy of dihydrogen nitride, $E_{T+osc}\left(^{14}NH_2\right)$.

Thus, E_D of $^{14}NH_2$ is given by:

$$E_D\left(^{14}NH_2\right) = E(H) + E(^{14}NH) - E_{T+osc}\left(^{14}NH_2\right) \quad (13.350)$$

where $E_T(^{14}NH)$ is given by the of the sum of the experimental energies of ^{14}N (Eq. (13.251)), H (Eq. (13.154)), and the negative of the bond energy of ^{14}NH (Eq. (13.312)):

$$E(^{14}NH) = -13.59844\ eV - 14.53414\ eV - 3.42\ eV = -31.55258\ eV \quad (13.351)$$

From Eqs. (13.154), (13.348), and (13.350-13.351), $E_D\left(^{14}NH_2\right)$ is

$$E_D\left(^{14}NH_2\right) = E(H) + E(^{14}NH) - E_{T+osc}\left(^{14}NH_2\right)$$
$$= -13.59844\ eV - 31.55258\ eV - \left(-49.08328\ eV\right) \quad (13.352)$$
$$= 3.9323\ eV$$

The experimental $^{14}NH_2$ bond dissociation energy from Ref. [34] and Ref. [35] is

$$E_D(^{14}NH_2) = 88 \pm 4\ kcal/mole = 3.8160\ eV \quad (13.353)$$

$$E_D(^{14}NH_2) = 91.0 \pm 0.5 \; kcal/mole = 3.9461 \; eV \tag{13.354}$$

Similarly, E_D of $^{14}ND_2$ is given by:

$$E_D\left(^{14}ND_2\right) = E(D) + E(^{14}ND) - \left(E_{T+osc}\left(^{14}ND_2\right)\right) \tag{13.355}$$

where $E_T(^{14}ND)$ is given by the of the sum of the experimental energies of ^{14}N (Eq. (13.251)), D (Eq. (13.155)), and the negative of the bond energy of ^{14}ND (Eq. (13.315)):

$$E(^{14}ND) = -13.603 \; eV - 14.53414 \; eV - 3.513 \; eV = -31.6506 \; eV \tag{13.356}$$

From Eqs. (13.155), (13.349), and (13.355-13.356), $E_D\left(^{14}ND_2\right)$ is

$$\begin{aligned} E_D(^{14}ND_2) &= -13.603 \; eV - 31.6506 \; eV - \left(-49.19366 \; eV\right) \\ &= 3.9401 \; eV \end{aligned} \tag{13.357}$$

The $^{14}ND_2$ bond dissociation energy calculated from the average of the experimental bond energies [34-35] and vibrational energy of $^{14}NH_2$ [33] is

$$\begin{aligned} E_D(^{14}ND_2) &= E_D(^{14}NH_2) + \frac{1}{2}\left(E_{vib}(^{14}NH_2) - E_{vib}(^{14}ND_2)\right) \\ &= \frac{1}{2}(3.8160 \; eV + 3.9461 \; eV) + \frac{1}{2}(0.40929 \; eV - 0.29890 \; eV) \\ &= 3.9362 \; eV \end{aligned} \tag{13.358}$$

BOND ANGLE OF NH_2

The NH_2 MO comprises a linear combination of two $N-H$ -bond MOs. Each $N-H$ -bond MO comprises the superposition of a H_2-type ellipsoidal MO and the $N2p_x$ AO or the $N2p_y$ AO with a relative charge density of 0.75 to 1.25; otherwise, the $N2p$ AOs are the same as those of the nitrogen atom. A bond is also possible between the two H atoms of the $N-H$ bonds. Such $H-H$ bonding would decrease the $N-H$ bond strength since electron density would be shifted from the $N-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $N-H$ bonds is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal H atoms of the $N-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{13.359}$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.360}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (13.167).

Since the two H_2-type ellipsoidal MOs comprise 75% of the H electron density of H_2 and the energy of each H_2-type ellipsoidal MO is matched to that of the $N2p$ AO; the component energies and the total energy E_T of the $H-H$ bond are given by Eqs. (13.67-13.73) except that V_e, T, and V_m are corrected for the energy matching factor of 0.93613 given in Eq. (13.248). Substitution of Eq. (13.359) into Eq. (13.233) with the energy-matching factor gives

$$0 = \left[\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[(0.93613)^{-1}\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right]\right]$$
$$+\frac{1}{2}\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o a^3}-\frac{e^2}{8\pi\varepsilon_o(a+c')^3}}{0.5m_p}}\Bigg] \tag{13.361}$$

From the energy relationship given by Eq. (13.361) and the relationship between the axes given by Eqs. (13.359-13.360) and (13.167-13.168), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (13.361) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 4.9500a_0 = 2.6194\,X\,10^{-10}\ m \tag{13.362}$$

Substitution of Eq. (13.362) into Eq. (13.359) gives

$$c' = 1.5732a_0 = 8.3251\,X\,10^{-11}\ m \tag{13.363}$$

The internuclear distance given by multiplying Eq. (13.363) by two is

$$2c' = 3.1464a_0 = 1.6650\,X\,10^{-10}\ m \tag{13.364}$$

Substitution of Eqs. (13.362-13.363) into Eq. (13.167) gives

$$b = c = 4.6933a_0 = 2.4836\,X\,10^{-10}\ m \tag{13.365}$$

Substitution of Eqs. (13.362-13.363) into Eq. (13.168) gives

$$e = 0.3178 \tag{13.366}$$

Using, $2c'_{H-H}$ (Eq. (13.364)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (13.361)), and $2c'_{N-H}$ (Eq. (13.325)), the internuclear distance of each $N-H$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle θ between the $N-H$ bonds is

$$\begin{aligned}\theta &= \cos^{-1}\left(\frac{2(1.9703)^2-(3.1464)^2}{2(1.9703)^2}\right) \\ &= \cos^{-1}(-0.2751) = 105.969^\circ\end{aligned} \tag{13.367}$$

The experimental angle between the $N-H$ bonds is [32]

$$\theta = 103.3^\circ \tag{13.368}$$

The results of the determination of bond parameters of NH_2 and ND_2 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

AMMONIA (NH_3)

Ammonia (NH_3) is formed by the reaction of a hydrogen atom with a dihydrogen nitride radical:

$$NH_2 + H \rightarrow NH_3 \tag{13.369}$$

NH_3 can be solved using the same principles as those used to solve NH_2 except that three rather than two H_2-type prolate spheroidal molecular orbitals (MOs) serve as basis functions in a linear combination with nitrogen atomic orbitals (AOs) to form the MO of NH_3.

FORCE BALANCE OF NH_3

NH_3 comprises three chemical bonds between nitrogen and hydrogen. Each $N-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the nitrogen atom and the other from the hydrogen atom. Each H-atom electron forms a H_2-type ellipsoidal MO with one of the initially unpaired N-atom electrons, $2p_x$, $2p_y$, or $2p_z$, such that the proton and the N nucleus serve as the foci. The initial N electron configuration given in the Seven-Electron Atoms section is $1s^2 2s^2 2p^3$, and the orbital

arrangement is given by Eqs. (10.134) and (13.246). The radius and the energy of the $N2p$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $N-H$ bond is provided by the spin-paring force of the NH_3 MO that has the symmetry of an s orbital that superimposes with the $N2p$ orbitals such that the corresponding angular momenta are unchanged.

As in the case of H_2, each of three $N-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the N atom for distances shorter than the radius of the $2p$ shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at each H proton that is continuous with the $2p$ shell at the N atom. The energies in the NH_3 MO involve only each $N2p$ and each $H1s$ electron with the formation of each $N-H$ bond. The sum of the energies of the prolate spheroids is matched to that of the $2p$ shell. The forces are determined by these energies. As in the cases of NH and NH_2, the linear combination of each H_2-type ellipsoidal MO with each $N2p$ AO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $N2p$ AO in order to match potential, kinetic, and orbital energy relationships. Thus, the NH_3 MO must comprise three $N-H$ bonds with each comprising 75% of a H_2-type ellipsoidal MO (1/2 +25%) and a nitrogen AO:

$$\left[1\,N2p_x\,AO+0.75\,H_2\,MO\right]+\left[1\,N2p_y\,AO+0.75\,H_2\,MO\right]+\left[1\,N2p_z\,AO+0.75\,H_2\,MO\right]\rightarrow NH_3\,MO \tag{13.370}$$

The force constant k' of the each H_2-type-ellipsoidal-MO component of the NH_3 MO is given by Eq. (13.248). The distance from the origin of each $N-H$-bond MO to each focus c' is given by Eq. (13.249). The internuclear distance is given by Eq. (13.250). The length of the semiminor axis of the prolate spheroidal $N-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $N-H$-bond MO. Since each of the three prolate spheroidal $N-H$-bond MOs comprises a H_2-type-ellipsoidal MO that transitions to the N AO, the energy E in Eq. (13.251) adds to that of the three corresponding H_2-type ellipsoidal MOs to give the total energy of the NH_3

MO. From the energy equation and the relationship between the axes, the dimensions of the NH_3 MO are solved.

The energy components of V_e, V_p, T, V_m, and E_T are three times those of OH and NH given by Eqs. (13.67-13.73) and 1.5 times those of H_2O given by Eqs. (13.172-13.178). Similarly to H_2O, since the each prolate spheroidal H_2-type MO transitions to the N AO and the energy of the $N2p$ shell must remain constant and equal to the negative of the ionization energy given by Eq. (13.251), the total energy $E_T(NH_3)$ of the NH_3 MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the N AO and the three H_2-type ellipsoidal MOs that forms the NH_3 MO as given by Eq. (13.370):

$$\begin{aligned} E_T(NH_2) &= E_T + E(2p\ shell) \\ &= E_T - E(ionization;\ N) \\ &= -3\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV \end{aligned} \tag{13.371}$$

The three hydrogen atoms and the nitrogen atom can achieve an energy minimum as a linear combination of three H_2-type ellipsoidal MOs each having the proton and the nitrogen nucleus as the foci. Each $N-H$-bond MO comprises the same $N2p$ shell of constant energy given by Eq. (13.251). Thus, an energy term of the NH_3 MO is given by the sum of the three H_2-type ellipsoidal MOs given by Eq. (11.212) minus the energy of the redundant nitrogen atom of the linear combination given by Eq. (13.251). The total sum is determined by the energy matching condition of the binding atoms.

In Eq. (13.248), the equipotential condition of the union of each H_2-type-ellipsoidal-MO and the N AO was met when the force constant used to determine the ellipsoidal parameter c' was normalized by the ratio of the ionization energy of N 14.53414 eV [6] and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). This normalized the force to match that of the Coulombic force alone to meet the force matching condition of the NH MO under the influence of the proton and the N nucleus. The minimum total energy of the NH_3 MO from the sum of energies of a linear combination from four atoms is determined using the energy matching condition of Eq. (13.248). Since each of the three prolate spheroidal $N-H$-bond MOs of NH_3 comprises a H_2-type-ellipsoidal MO that transitions to the N AO and the energy matching

condition is met, the nitrogen energy E (Eq. (13.251)) and the energy (Eq. (1.243)) of a hydrogen atomic orbital (H AO), $E_{Coulomb}(H)$, corresponding to the Coulombic force of $+e$ from the nitrogen nucleus is subtracted from the sum of the energies of the three corresponding H_2-type ellipsoidal MOs to given an energy minimum. From another perspective, the electron configuration of NH_2 is equivalent to that of OH and is given by Eq. (10.174). NH_2 serves as a one-electron atom that is energy matched by the H AO as a basis element to minimize the energy of NH_3 in the formation of the third $N-H$ -bond.

$$E_T(3H_2-N-H)=\left\{\begin{matrix}-3\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]\\ -E(N2p\ shell)-E_{Coulomb}(H)\end{matrix}\right\}$$
$$=3(-31.63536831\ eV)-(-14.53414\ eV-13.605804eV) \quad (13.372)$$
$$=-66.76616\ eV$$

$E_T(NH_3)$ given by Eq. (13.371) is set equal to Eq. (13.372), three times the energy of the H_2-type ellipsoidal MO minus the energy of the $N2p$ shell and the H AO:

$$E_T(NH_3)=-3\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV=-66.76616\ eV \quad (13.373)$$

From the energy relationship given by Eq. (13.373) and the relationship between the axes given by Eqs. (13.248-13.250) and (13.62-13.63), the dimensions of the NH_3 MO can be solved.

Substitution of Eq. (13.249) into Eq. (13.373) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{0.712154aa_0}}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{0.712154aa_0}}{a-\sqrt{0.712154aa_0}}-1\right]=e52.23202 \quad (13.374)$$

The most convenient way to solve Eq. (13.374) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.34750a_0=7.13066\,X\,10^{-11}\ m \quad (13.375)$$

Substitution of Eq. (13.375) into Eq. (13.249) gives

$$c'=0.97961a_0=5.18385\,X\,10^{-11}\ m \quad (13.376)$$

The internuclear distance given by multiplying Eq. (13.376) by two is

$$2c'=1.95921a_0=1.03677\,X\,10^{-10}\ m \quad (13.377)$$

The experimental bond distance is [32]

$$2c' = 1.012\,X\,10^{-10}\ m \tag{13.378}$$

Substitution of Eqs. (13.375-13.376) into Eq. (13.62) gives

$$b = c = 0.92527a_0 = 4.89633\,X\,10^{-11}\ m \tag{13.379}$$

Substitution of Eqs. (13.375-13.376) into Eq. (13.63) gives

$$e = 0.72698 \tag{13.380}$$

The nucleus of the H atom and the nucleus of the N atom comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of each H_2-type ellipsoidal MO and the $N2p_x$, $N2p_y$, or $N2p_z$ AO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.261-13.270). Using Eqs. (13.375-13.377) and (13.379-13.380), the polar intersection angle θ' given by Eq. (13.261) with $r_n = r_7 = 0.93084a_0$ is

$$\theta' = 115.89° \tag{13.381}$$

Then, the angle θ_{N2pAO} the radial vector of the $N2p_x$, $N2p_y$, or $N2p_z$ AO makes with the internuclear axis is

$$\theta_{N2pAO} = 180° - 115.89° = 64.11° \tag{13.382}$$

as shown in Figure 10. The angle θ_{H_2MO} between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the N radial vector given by Eqs. (13.264-13.265), (13.379), and (13.382) is

$$\theta_{H_2MO} = 64.83° \tag{13.383}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.267), (13.375), and (13.383) is

$$d_{H_2MO} = 0.57314a_0 = 3.03292\,X\,10^{-11}\ m \tag{13.384}$$

The distance d_{N2pAO} along the internuclear axis from the origin of the N atom to the point of intersection of the orbitals given by Eqs. (13.269), (13.376), and (13.384) is

$$d_{N2pAO} = 0.40647a_0 = 2.15093\,X\,10^{-11}\ m \tag{13.385}$$

As shown in Eq. (13.370), in addition to the p-orbital charge-density modulation, the uniform charge-density in the p_x, p_y, and p_z orbitals is increased by a factor of 0.25 and the H atoms are each decreased by a factor of 0.25. Using the orbital composition of NH_3 (Eq.

(13.370)), the radii of $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), and $N2p = 0.93084a_0$ (Eq. (10.142)) shells, and the parameters of the NH_3 MO given by Eqs. (13.3-13.4) and (13.375-13.385), the charge-density of the NH_3 MO comprising the linear combination of three $N-H$ -bond MOs (NH -type ellipsoidal MOs given in the Energies of NH section) according to Eq. (13.370) is shown in Figure 13. Each $N-H$ -bond MO comprises a H_2-type ellipsoidal MO and an $N2p$ AO having the dimensional diagram shown in Figure 10.

ENERGIES OF NH_3

The energies of NH_3 given by the substitution of the semiprincipal axes ((Eqs. (13.375-13.377) and (13.379)) into the energy equations (Eqs. (13.67-13.73)) multiplied by three are

$$V_e = 3\left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -115.28799\ eV \tag{13.386}$$

$$V_p = 3\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 41.66718\ eV \tag{13.387}$$

$$T = 3\left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 42.77848\ eV \tag{13.388}$$

$$V_m = 3\left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -21.38924\ eV \tag{13.389}$$

$$E_T(NH_3) = -3\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV = -66.76571\ eV \tag{13.390}$$

where $E_T(NH_3)$ is given by Eq. (13.371) which is reiteratively matched to Eq. (13.372) within five-significant-figure round-off error.

VIBRATION OF NH_3

The vibrational energy levels of NH_3 may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as

given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERM OF NH_3

The radiation reaction force in the case of the vibration of NH_3 in the transition state corresponds to the Doppler energy, E_D, given by Eq. (11.181) and Eqs. (13.22) and (13.144) that is dependent on the motion of the electrons and the nuclei. The kinetic energy of the transient vibration is derived from the corresponding central forces. The equations of the radiation reaction force of ammonia are the same as those of the corresponding water and dihydrogen and dideuterium nitride radicals with the substitution of the ammonia parameters. Using Eqs. (11.136) and (13.207-13.209), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\left(\frac{3}{2}\right)\frac{e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 5.68887\,X\,10^{16}\ rad/s \tag{13.391}$$

where b is given by Eq. (13.379). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 5.68887\,X\,10^{16}\ rad/s = 37.44514\ eV \tag{13.392}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO acting independently due to the D_{3h} symmetry point group, for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.392) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.6353683\ eV\sqrt{\frac{2e(37.44514\ eV)}{m_e c^2}} = -0.38298\ eV \tag{13.393}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of NH_3 due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.393) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational

energy of NH_3. Using the experimental $^{14}NH_3$ vibrational energy of $E_{vib} = 3443.59\ cm^{-1} = 0.426954\ eV$ [36] gives

$$\overline{E}'_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.394}$$

$$\overline{E}'_{osc} = -0.38298\ eV + \frac{1}{2}(0.426954\ eV) = -0.16950\ eV \tag{13.395}$$

per bond. The reentrant orbit for the binding of a hydrogen atom to a NH_2 radical involves three $N-H$ bonds. Since the vibration and reentrant oscillation is along three bonds, $\overline{E}_{osc}$ for $^{14}NH_3$, $\overline{E}_{osc}\left(^{14}NH_3\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left(^{14}NH_3\right) &= 3\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 3\left(-0.38298\ eV + \frac{1}{2}(0.426954\ eV)\right)\\ &= -0.50850\ eV\end{aligned} \tag{13.396}$$

Using Eq. (13.393), Eqs. (13.394-13.396), and the $^{14}ND_3$ experimental vibrational energy of $E_{vib} = 2563.96\ cm^{-1} = 0.317893\ eV$ [36], the corresponding $\overline{E}_{osc}\left(^{14}ND_2\right)$ is

$$\begin{aligned}\overline{E}_{osc}\left(^{14}ND_3\right) &= 3\left(-0.38298\ eV + \frac{1}{2}(0.317893\ eV)\right)\\ &= -0.67209\ eV\end{aligned} \tag{13.397}$$

TOTAL AND BOND ENERGIES OF $^{14}NH_3$ AND $^{14}ND_3$

$E_{T+osc}\left(^{14}NH_3\right)$, the total energy of the $^{14}NH_3$ including the Doppler term, is given by the sum of $E_T(NH_3)$ (Eq. (13.373)) and $\overline{E}_{osc}\left(^{14}NH_3\right)$ given Eqs. (13.391-13.396):

$$\begin{aligned}E_{T+osc}\left(^{14}NH_3\right) &= V_e + T + V_m + V_p + E(N2p) + \overline{E}_{osc}\left(^{14}NH_3\right)\\ &= E_T(NH_3) + \overline{E}_{osc}\left(^{14}NH_3\right)\end{aligned} \tag{13.398}$$

$$E_{T+osc}\left({}^{14}NH_3\right)=\left\{\begin{array}{l}\left(3\frac{-e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.53414\ eV\right)\\ -3\left(\left(31.63536831\ eV\right)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{2}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}}{m_e c^2}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\} \qquad (13.399)$$

$$=-66.76616\ eV-3\left(0.38298\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

From Eqs. (13.396) and (13.398-13.399), the total energy of ${}^{14}NH_2$ is

$$\begin{aligned}E_{T+osc}\left({}^{14}NH_3\right)&=-66.76616\ eV+\overline{E}_{osc}\left({}^{14}NH_3\right)\\&=-66.76616\ eV-3\left(0.38298\ eV-\frac{1}{2}\left(0.426954\ eV\right)\right)\\&=-67.27466\ eV\end{aligned} \qquad (13.400)$$

where the experimental ${}^{14}NH_3$ vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

$E_{T+osc}\left({}^{14}ND_3\right)$, the total energy of ${}^{14}ND_3$ including the Doppler term is given by the sum of $E_T\left(ND_3\right)=E_T\left(NH_3\right)$ (Eq. (13.373)) and $\overline{E}_{osc}\left({}^{14}ND_3\right)$ given by Eq. (13.397):

$$\begin{aligned}E_{T+osc}\left({}^{14}ND_3\right)&=-66.76616\ eV+\overline{E}_{osc}\left({}^{14}ND_3\right)\\&=-66.76616\ eV-3\left(0.38298\ eV-\frac{1}{2}\left(0.317893\ eV\right)\right)\\&=-67.43780\ eV\end{aligned} \qquad (13.401)$$

where the experimental ${}^{14}ND_3$ vibrational energy was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. The corresponding bond dissociation energy, E_D, is given by the sum of the total energies of the corresponding dihydrogen nitride radical and hydrogen atom minus the total energy of ammonia, $E_{T+osc}\left({}^{14}NH_3\right)$.

Thus, E_D of ${}^{14}NH_3$ is given by:

$$E_D\left({}^{14}NH_3\right)=E(H)+E({}^{14}NH_2)-E_{T+osc}\left({}^{14}NH_3\right) \qquad (13.402)$$

where $E_T({}^{14}NH_2)$ is given by the of the sum of the experimental energies of ${}^{14}N$ (Eq. (13.251)), two H (Eq. (13.154)), and the negative of the bond energies of ${}^{14}NH$ (Eq. (13.312)) and ${}^{14}NH_2$ (Eq. (13.354)):

$$E(^{14}NH_2) = 2(-13.59844\ eV) - 14.53414\ eV - 3.42\ eV - 3.946\ eV = -49.09709\ eV \tag{13.403}$$

From Eqs. (13.154), (13.400), and (13.402-13.403), $E_D\left(^{14}NH_2\right)$ is

$$\begin{aligned} E_D\left(^{14}NH_3\right) &= E(H) + E(^{14}NH_2) - E_{T+osc}\left(^{14}NH_3\right) \\ &= -13.59844\ eV - 49.09709\ eV - (-67.27466\ eV) \\ &= 4.57913\ eV \end{aligned} \tag{13.404}$$

The experimental $^{14}NH_3$ bond dissociation energy [37] is

$$E_D(^{14}NH_3) = 4.60155\ eV \tag{13.405}$$

Similarly, E_D of $^{14}ND_3$ is given by:

$$E_D\left(^{14}ND_3\right) = E(D) + E(^{14}ND_2) - \left(E_{T+osc}\left(^{14}ND_3\right)\right) \tag{13.406}$$

where $E_T(^{14}ND_2)$ is given by the of the sum of the experimental energies of ^{14}N (Eq. (13.251)), two times the energy of D (Eq. (13.155)), and the negative of the bond energies of ^{14}ND (Eq. (13.315)) and $^{14}ND_2$ (Eq. (13.358)):

$$E(^{14}ND_2) = 2(-13.603\ eV) - 14.53414\ eV - 3.5134\ eV - 3.9362\ eV = -49.18981\ eV \tag{13.407}$$

From Eqs. (13.155), (13.401), and (13.406-13.407), $E_D\left(^{14}ND_3\right)$ is

$$E_D(^{14}ND_3) = -13.603\ eV - 49.18981\ eV - (-67.43780\ eV) = 4.64499\ eV \tag{13.408}$$

The experimental $^{14}ND_3$ bond dissociation energy [37] is

$$E_D(^{14}ND_3) = 4.71252\ eV \tag{13.409}$$

BOND ANGLE OF NH_3

Using, $2c'_{H-H}$ (Eq. (13.364)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (13.361)), and $2c'_{N-H}$, the internuclear distance of each $N-H$ bond (Eq. (13.377)), the corresponding bond angle can be determined from the law of cosines. Using Eq. (13.367), the bond angle θ between the $N-H$ bonds is

$$\theta = \cos^{-1}\left(\frac{2(1.95921)^2 - (3.14643)^2}{2(1.95921)^2}\right) = \cos^{-1}(-0.28956) = 106.67^\circ \tag{13.410}$$

The experimental angle between the $N-H$ bonds is [36]

$$\theta = 106.67° \tag{13.411}$$

The NH_3 molecule has a pyramidal structure with the nitrogen atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. Since any two $N-H$ bonds form an isosceles triangle, the distance $d_{origin-H}$ from the origin to the nucleus of a hydrogen atom is given by

$$d_{origin-H} = \frac{2c'_{H-H}}{2\sin 60°} \tag{13.412}$$

Substitution of Eq. (13.364) into Eq. (13.412) gives

$$d_{origin-H} = 1.81659a_0 \tag{13.413}$$

The height along the z-axis of the pyramid from the origin to N nucleus d_{height} is given by

$$d_{height} = \sqrt{\left(2c'_{N-H}\right)^2 - \left(d_{origin-H}\right)^2} \tag{13.414}$$

Substitution of Eqs. (13.377) and (13.413) into Eq. (13.414) gives

$$d_{height} = 0.73383a_0 \tag{13.415}$$

The angle θ_v of each $N-H$ bond from the z-axis is given by

$$\theta_v = \tan^{-1}\left(\frac{d_{origin-H}}{d_{height}}\right) \tag{13.416}$$

Substitution of Eqs. (13.413) and (13.415) into Eq. (13.417) gives

$$\theta_v = 68.00° \tag{13.417}$$

The NH_3 MO shown in Figure 13 was rendered using these parameters.

The results of the determination of bond parameters of NH_3 and ND_3 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

HYDROGEN CARBIDE (CH)

The methane molecule can be solved by first considering the solution of the hydrogen carbide, dihydrogen carbide, and methyl radicals. The former is formed by the reaction of a hydrogen atom and a carbon atom:

$$H + C \rightarrow CH \tag{13.418}$$

The hydrogen carbide radicals, CH and CH_2, methyl radical, CH_3, and methane, CH_4, can be solved using the same principles as those used to solve OH, H_2O, NH, NH_2, and NH_3 with the exception that the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum.

FORCE BALANCE OF CH

CH comprises two spin-paired electrons in a chemical bond between the carbon atom and the hydrogen atom. The CH radical molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal H_2 MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, the H-atom electron forms a H_2-type ellipsoidal MO with one of the C-atom electrons. However, such a bond is not possible with the outer C electrons in their ground state since the resulting H_2-type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon $2p$ shell, which is not energetically stable. Thus, when bonding the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum.

The C electron configuration given in the Six-Electron Atoms section is $1s^2 2s^2 2p^2$, and the orbital arrangement is

$$\begin{array}{ccc} & \text{2p state} & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\quad} \\ 1 & 0 & -1 \end{array} \tag{13.419}$$

corresponding to the ground state ${}^3P_0$. The radius r_6 of the $2p$ shell given by Eq. (10.122) is

$$r_6 = 1.20654 a_0 \tag{13.420}$$

The energy of the carbon $2p$ shell is the negative of the ionization energy of the carbon atom given by Eq. (10.123). Experimentally, the energy is [12]

$$E(C, 2p\ shell) = -E(ionization;\ C) = -11.2603\ eV \tag{13.421}$$

The $C2s$ atomic orbital (AO) combines with the $C2p$ AOs to form a single $2sp^3$ hybridized orbital (HO) with the orbital arrangement

$$\begin{array}{cccc} & & 2sp^3 \text{ state} & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \tag{13.422}$$

where the quantum numbers (ℓ, m_ℓ) are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C,2sp^3\right)$ of calculated energies of C, C^+, C^{2+}, and C^{3+} from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$E_T\left(C,2sp^3\right)=64.3921\ eV+48.3125\ eV+24.2762\ eV+11.27671\ eV=148.25751\ eV \tag{13.423}$$

which agrees well with the sum of $148.02532\ eV$ from the experimental [6] values. The orbital-angular-momentum interactions cancel such that the energy of the $E_T\left(C,2sp^3\right)$ is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius r_{2sp^3} of the $C2sp^3$ shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{2sp^3}=\sum_{n=2}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)}=\frac{10e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)}=0.91771a_0 \tag{13.424}$$

Using Eqs. (10.102) and (13.424), the Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E_{Coulomb}\left(C,2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.91771a_0}=-14.82575\ eV \tag{13.425}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152) at the initial radius of the $2s$ electrons. From Eq. (10.62) with $Z=6$, the radius r_3 of $C2s$ shell is

$$r_3=0.84317a_0 \tag{13.426}$$

Using Eqs. (13.152) and (13.426), the unpairing energy is

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}=\frac{8\pi\mu_o\mu_B^2}{\left(0.84317a_0\right)^3}=0.19086\ eV \tag{13.427}$$

Using Eqs. (13.425) and (13.427), the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$

shell is

$$E\left(C,2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}$$
$$=-14.82575\ eV+0.19086\ eV \quad (13.428)$$
$$=-14.63489\ eV$$

The nitrogen atom's $2p$-shell electron configuration given by Eq. (10.134) is the same as that of the $C2sp^3$ shell, and nitrogen's calculated energy of $14.61664\ eV$ given by Eq. (10.143) is a close match with $E\left(C,2sp^3\right)$. Thus, the binding should be very similar except that four bonds to hydrogen can occur with carbon.

The carbon $C2sp^3$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the H atom and the nucleus of the C atom are along the internuclear axis and serve as the foci. Due to symmetry, the other C electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the CH MO involve only the $C2sp^3$ and $H1s$ electrons. The forces are determined by these energies.

As in the case of H_2, the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell. Thus, the MO surface comprises a prolate spheroid at the H proton that is continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus. The energy of the H_2-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case with OH and NH, the linear combination of the H_2-type ellipsoidal MO with the $C2sp^3$ HO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $C2sp^3$ HO in order to match potential, kinetic, and orbital energy relationships. Thus, the CH MO must comprise 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO:

$$1\ C2sp^3+0.75\ H_2\ MO\rightarrow CH\ MO \quad (13.429)$$

The force balance of the CH MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.429) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

As in the case with OH (Eq. (13.57)), the H_2-type ellipsoidal MO comprises 75% of the CH MO; so, the electron charge density in Eq. (11.65) is given by $-0.75e$. The force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the CH MO. Since the CH MO comprises a H_2-type-ellipsoidal MO that transitions to the $C2sp^3$ HO, the energy $E\left(C,2sp^3\right)$ in Eq. (13.428) adds to that of the H_2-type ellipsoidal MO to give the total energy of the CH MO. From the energy equation and the relationship between the axes, the dimensions of the CH MO are solved.

The energy components of V_e, V_p, T, and V_m are those of H_2 (Eqs. (11.207-11.212)) except that they are corrected for electron hybridization. Hybridization gives rise to the $C2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425). To meet the equipotential condition of the union of the H_2-type-ellipsoidal-MO and the $C2sp^3$ HO, the electron energies are normalized by the ratio of $14.82575\,eV$, the magnitude of $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425), and $13.605804\,eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). This normalizes the energies to match that of the Coulombic energy alone to meet the energy matching condition of the CH MO under the influence of the proton and the C nucleus. The hybridization energy factor C_{C2sp^3HO} is

$$C_{C2sp^3HO}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{2sp^3}}}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.91771 a_0}}=\frac{13.605804\,eV}{14.82575\,eV}=0.91771 \tag{13.430}$$

The total energy $E_T\left(CH\right)$ of the CH MO is given by the sum of the energies of the orbitals, the H_2-type ellipsoidal MO and the $C2sp^3$ HO, that form the hybridized CH MO. $E_T\left(CH\right)$ follows from by Eq. (13.74) for OH, but the energy of the $C2sp^3$ HO given by Eq. (13.428) is substituted for the energy of O and the H_2-type-ellipsoidal-MO energies are

those of H_2 (Eqs. (11.207-11.212)) multiplied by the electron hybridization factor rather than by the factor of 0.75:

$$E_T(CH) = E_T + E(C,2sp^3) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV \quad (13.431)$$

To match the boundary condition that the total energy of the entire the H_2-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_T(CH)$ given by Eq. (13.431) is set equal to Eq. (13.75):

$$E_T(CH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -31.63536831\ eV \quad (13.432)$$

From the energy relationship given by Eq. (13.432) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.432) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e17.00048 \quad (13.433)$$

The most convenient way to solve Eq. (13.433) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.67465a_0 = 8.86186\,X\,10^{-11}\ m \quad (13.434)$$

Substitution of Eq. (13.434) into Eq. (13.60) gives

$$c' = 1.05661a_0 = 5.59136\,X\,10^{-11}\ m \quad (13.435)$$

The internuclear distance given by multiplying Eq. (13.435) by two is

$$2c' = 2.11323a_0 = 1.11827\,X\,10^{-10}\ m \quad (13.436)$$

The experimental bond distance is [14]

$$2c' = 1.1198\,X\,10^{-10}\ m \quad (13.437)$$

Substitution of Eqs. (13.434-13.435) into Eq. (13.62) gives

$$b = c = 1.29924a_0 = 6.87527\,X\,10^{-11}\ m \quad (13.438)$$

Substitution of Eqs. (13.434-13.435) into Eq. (13.63) gives

$$e = 0.63095 \quad (13.439)$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{2sp^3} = 0.91771a_0$ is the radius of the $C2sp^3$ shell. Substitution of Eqs. (13.434-13.435) into Eq. (13.261) gives

$$\theta' = 81.03° \tag{13.440}$$

Then, the angle θ_{C2sp^3HO} the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180° - 81.03° = 98.97° \tag{13.441}$$

as shown in Figure 14.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C2sp^3$ radial vector obeys the following relationship:

$$r_{2sp^3} \sin\theta_{C2sp^3HO} = 0.91771a_0 \sin\theta_{C2sp^3HO} = b\sin\theta_{H_2MO} \tag{13.442}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.91771a_0 \sin\theta_{C2sp^3HO}}{b} = \sin^{-1}\frac{0.91771a_0 \sin 98.97°}{b} \tag{13.443}$$

with the use of Eq. (13.441). Substitution of Eq. (13.438) into Eq. (13.443) gives

$$\theta_{H_2MO} = 44.24° \tag{13.444}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.445}$$

Substitution of Eqs. (13.434) and (13.444) into Eq. (13.445) gives

$$d_{H_2MO} = 1.19968a_0 = 6.34845\ X\ 10^{-11}\ m \tag{13.446}$$

The distance d_{C2sp^3HO} along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C2sp^3HO} = d_{H_2MO} - c' \tag{13.447}$$

Substitution of Eqs. (13.435) and (13.446) into Eq. (13.447) gives

$$d_{C2sp^3HO} = 0.14307a_0 = 7.57090\,X\,10^{-12}\ m \tag{13.448}$$

As shown in Eq. (13.429), the uniform charge-density in the $C2sp^3$ HO is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25. Using the orbital composition of CH (Eq. (13.429)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C2sp^3 = 0.91771a_0$ (Eq. (10.424)) shells, and the parameters of the CH MO given by Eqs. (13.3-13.4), (13.434-13.436), and (13.438-13.448), the dimensional diagram and charge-density of the CH MO comprising the linear combination of the H_2-type ellipsoidal MO and the $C2sp^3$ HO according to Eq. (13.429) are shown in Figures 14 and 15, respectively.

ENERGIES OF CH

The energies of CH are given by the substitution of the semiprincipal axes (Eqs. (13.434-13.435) and (13.438)) into the energy equations, (Eq. (13.431) and Eqs. (11.207-11.211) that are corrected for electron hybridization using Eq. (13.430):

$$V_e = (0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -35.12015\ eV \tag{13.449}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 12.87680\ eV \tag{13.450}$$

$$T = (0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 10.48582\ eV \tag{13.451}$$

$$V_m = (0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -5.24291\ eV \tag{13.452}$$

$$E_T(CH) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -31.63533\ eV \tag{13.453}$$

where $E_T(CH)$ is given by Eq. (13.431) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

VIBRATION AND ROTATION OF CH

The vibrational energy of CH may be solved in the same manner as that of OH and NH except that the force between the electrons and the foci given by Eq. (13.102) is doubled due to electron hybridization of the two shells of carbon after Eq. (11.141). From Eqs. (13.102-13.106) with the substitution of the CH parameters, the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3} - \frac{e^2}{8\pi\varepsilon_0 (2c')^3}}{\mu}}$$
$$= \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 (1.29924a_0)^3} - \frac{e^2}{8\pi\varepsilon_0 (2.11323a_0)^3}}{\frac{12}{13}m_p}} \tag{13.454}$$
$$= 5.39828\ X\ 10^{14}\ rad/s$$

where b is given by Eq. (13.438), $2c'$ is given by Eq. (13.436), and the reduced mass of ^{12}CH is given by:

$$\mu_{^{12}CH} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1)(12)}{1+12} m_p \tag{13.455}$$

where m_p is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for ^{12}CH given by Eqs. (11.136), (11.148), and (13.454) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{449.94\ Nm^{-1}}{\mu}} = 5.39828\ X\ 10^{14}\ radians/s \tag{13.456}$$

where the reduced nuclear mass of ^{12}CH is given by Eq.(13.455) and the spring constant, $k(0)$, given by Eqs. (11.136) and (13.454) is

$$k(0) = 449.94\ Nm^{-1} \tag{13.457}$$

The ^{12}CH transition-state vibrational energy, $E_{vib}(0)$, given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \hbar\omega = \hbar 5.39828\ X\ 10^{14}\ rad/s = 0.35532\ eV = 2865.86\ cm^{-1} \tag{13.458}$$

ω_e, from the experimental curve fit of the vibrational energies of ^{12}CH is [14]

$$\omega_e = 2861.6\ cm^{-1} \tag{13.459}$$

Using Eqs. (13.112-13.118) with $E_{vib}(0)$ given by Eq. (13.458) and D_0 given by Eq. (13.488), the ^{12}CH $\upsilon = 1 \rightarrow \upsilon = 0$ vibrational energy, $E_{vib}(1)$ is

$$E_{vib}(1) = 0.33879\ eV \qquad \left(2732.61\ cm^{-1}\right) \tag{13.460}$$

The experimental vibrational energy of ^{12}CH using ω_e and $\omega_e x_e$ [14] according to K&P [15] is

$$E_{vib}(1) = 0.33885\ eV \qquad \left(2733\ cm^{-1}\right) \tag{13.461}$$

Using Eq. (13.113) with $E_{vib}(1)$ given by Eq. (13.460) and D_0 given by Eq. (13.488), the anharmonic perturbation term, $\omega_0 x_0$, of ^{12}CH is

$$\omega_0 x_0 = 66.624\ cm^{-1} \tag{13.462}$$

The experimental anharmonic perturbation term, $\omega_0 x_0$, of ^{12}CH [14] is

$$\omega_0 x_0 = 64.3\ cm^{-1} \tag{13.463}$$

The vibrational energies of successive states are given by Eqs. (13.458), (13.112), and (13.462).

Using b given by Eq. (13.438), $2c'$ given by Eq. (13.436), D_0 given by Eq. (13.490), and the reduced nuclear mass of ^{12}CD given by

$$\mu_{^{12}CD} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(12)}{2+12} m_p \tag{13.464}$$

where m_p is the proton mass, the corresponding parameters for deuterium carbide ^{12}CD (Eqs. (13.102-13.121)) are

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{449.94\ Nm^{-1}}{\mu}} = 3.96126\ X\ 10^{14}\ radians/s \tag{13.465}$$

$$k(0) = 449.94\ Nm^{-1} \tag{13.466}$$

$$E_{vib}(0) = \hbar\omega = \hbar 3.96126\ X\ 10^{14}\ rad/s = 0.26074\ eV = 2102.97\ cm^{-1} \tag{13.467}$$

$$E_{vib}(1) = 0.25173\ eV \qquad \left(2030.30\ cm^{-1}\right) \tag{13.468}$$

$$\omega_0 x_0 = 36.335\ cm^{-1} \tag{13.469}$$

ω_e, from the experimental curve fit of the vibrational energies of ^{12}CD is [14]

$$\omega_e = 2101.0\ cm^{-1} \tag{13.470}$$

The experimental vibrational energy of ^{12}CD using ω_e and $\omega_e x_e$ [14] according to K&P [15] is

$$E_{vib}(1) = 0.25189\ eV \qquad \left(2031.6\ cm^{-1}\right) \tag{13.471}$$

and the experimental anharmonic perturbation term, $\omega_0 x_0$, of ^{12}CD is [14]

$$\omega_0 x_0 = 34.7\ cm^{-1} \tag{13.472}$$

which match the predictions given by Eqs. (13.467), (13.468) and (13.469), respectively.

Using Eqs. (13.133-13.134) and the internuclear distance, $r = 2c'$, and reduced mass of ^{12}CH given by Eqs. (13.436) and (13.455), respectively, the corresponding B_e is

$$B_e = 14.498\ cm^{-1} \tag{13.473}$$

The experimental B_e rotational parameter of ^{12}CH is [14]

$$B_e = 14.457\ cm^{-1} \tag{13.474}$$

Using the internuclear distance, $r = 2c'$, and reduced mass of ^{12}CD given by Eqs. (13.436) and (13.464), respectively, the corresponding B_e is

$$B_e = 7.807\ cm^{-1} \tag{13.475}$$

The experimental B_e rotational parameter of ^{12}CD is [14]

$$B_e = 7.808\ cm^{-1} \tag{13.476}$$

THE DOPPLER ENERGY TERMS OF ^{12}CH AND ^{12}CD

The equations of the radiation reaction force of hydrogen and deuterium carbide are the same as those of the corresponding hydroxyl and hydrogen nitride radicals with the substitution of the hydrogen and deuterium carbide parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.41759\ X\ 10^{16}\ rad/s \tag{13.477}$$

where b is given by Eq. (13.438). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.41759\ X\ 10^{16}\ rad/s = 15.91299\ eV \tag{13.478}$$

In Eq. (11.181), substitution of the total energy of CH, $E_T(CH)$, (Eq. (13.432)) for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.478) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(15.91299\ eV)}{m_e c^2}} = -0.24966\ eV \tag{13.479}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.479) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of CH. The experimental ^{12}CH ω_e is $2861.6\ cm^{-1}$ $(0.35480\ eV)$ [14] which matches the predicted ω_e of $2865.86\ cm^{-1}$ $(0.35532\ eV)$ given by Eq. (13.458). Using the predicted ω_e for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(^{12}CH)$ is

$$\overline{E}_{osc}(^{12}CH) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.480}$$

$$\overline{E}_{osc}(^{12}CH) = -0.24966\ eV + \frac{1}{2}(0.35532\ eV) = -0.07200\ eV \tag{13.481}$$

The experimental ^{12}CD ω_e is $2101.0\ cm^{-1}$ $(0.26049\ eV)$ [14] which matches the predicted ω_e of $2102.97\ cm^{-1}$ $(0.26074\ eV)$ given by Eq. (13.467). Using Eq. (13.479) and the predicted ω_e for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(^{12}CD)$ is

$$\overline{E}_{osc}(^{12}CD) = -0.24966\ eV + \frac{1}{2}(0.26074\ eV) = -0.11929\ eV \tag{13.482}$$

TOTAL AND BOND ENERGIES OF ^{12}CH AND ^{12}CD

$E_{T+osc}(^{12}CH)$, the total energy of the ^{12}CH radical including the Doppler term, is given by the sum of $E_T(CH)$ (Eq. (13.432)) and $\overline{E}_{osc}(^{12}CH)$ given by Eq. (13.481):

$$\begin{aligned} E_{T+osc}(^{12}CH) &= V_e + T + V_m + V_p + E(C, 2sp^3) + \overline{E}_{osc}(^{12}CH) \\ &= E_T(CH) + \overline{E}_{osc}(^{12}CH) \end{aligned} \tag{13.483}$$

$$E_{T+osc}\left({}^{12}CH\right)=\left\{\begin{array}{l}\left(\frac{-e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV\right)\\ \left(1+\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}{m_e c^2}}\right)+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\end{array}\right\}$$

$$=-31.63537\ eV-0.24966\ eV+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \qquad (13.484)$$

From Eqs. (13.480-13.481) and (13.483-13.484), the total energy of ${}^{12}CH$ is

$$\begin{aligned}E_{T+osc}\left({}^{12}CH\right)&=-31.63537\ eV+\bar{E}_{osc}\left({}^{12}CH\right)\\&=-31.63537\ eV-0.24966\ eV+\frac{1}{2}(0.35532\ eV)\\&=-31.70737\ eV\end{aligned} \qquad (13.485)$$

where the predicted ω_e (Eq. (13.458)) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term. $E_{T+osc}\left({}^{12}CD\right)$, the total energy of ${}^{12}CD$ including the Doppler term, is given by the sum of $E_T(CD)=E_T(CH)$ (Eq. (13.432)) and $\bar{E}_{osc}\left({}^{12}CD\right)$ given by Eq. (13.482):

$$\begin{aligned}E_{T+osc}\left({}^{12}CD\right)&=-31.63537\ eV+\bar{E}_{osc}\left({}^{12}CD\right)\\&=-31.63537\ eV-0.24966\ eV+\frac{1}{2}(0.26074\ eV)\\&=-31.75462\ eV\end{aligned} \qquad (13.486)$$

where the predicted ω_e (Eq. (13.467)) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The CH bond dissociation energy, $E_D\left({}^{12}CH\right)$, is given by the sum of the total energies of the $C2sp^3$ HO and the hydrogen atom minus $E_{T+osc}\left({}^{12}CH\right)$[3]:

$$E_D\left({}^{12}CH\right)=E\left(C,2sp^3\right)+E(H)-E_{T+osc}\left({}^{12}CH\right) \qquad (13.487)$$

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[3] The hybridization energy is the difference between and $E\left(C,2sp^3\right)$ given by Eq. (13.428) and $E\left(C,2p\ shell\right)$ given by Eq. (13.421). Since this term adds to $E\left(C,2p\ shell\right)$ to give the total energy from which $E_{T+osc}\left({}^{12}CH\right)$ is subtracted to give $E_D\left({}^{12}CH\right)$, it is more convenient to simply use $E\left(C,2sp^3\right)$directly in Eq. (13.487).

$E\left(C,2sp^3\right)$ is given by Eq. (13.428), and $E_D(H)$ is given by Eq. (13.154). Thus, the ^{12}CH bond dissociation energy, $E_D\left(^{12}CH\right)$, given by Eqs. (13.154), (13.428), (13.485), and (13.487) is

$$\begin{aligned} E_D\left(^{12}CH\right) &= -\left(14.63489\ eV + 13.59844\ eV\right) - E_{T+osc}(CH) \\ &= -28.23333\ eV - \left(-31.70737\ eV\right) \\ &= 3.47404\ eV \end{aligned} \tag{13.488}$$

The experimental ^{12}CH bond dissociation energy is [14]

$$E_D\left(^{12}CH\right) = 3.47\ eV \tag{13.489}$$

which is a close match to that of NH as predicted based on the match between the N and $C2sp^3$ HO energies and electron configurations.

The ^{12}CD bond dissociation energy, $E_D\left(^{12}CD\right)$, is given by the sum of the total energies of the $C2sp^3$ HO and the deuterium atom minus $E_{T+osc}(CD)$:

$$E_D\left(^{12}CD\right) = E\left(C,2sp^3\right) + E(D) - E_{T+osc}\left(^{12}CD\right) \tag{13.490}$$

$E\left(C,2sp^3\right)$ is given by Eq. (13.428), and $E_D(D)$ is given by Eq. (13.155). Thus, the ^{12}CD bond dissociation energy, $E_D\left(^{12}CD\right)$, given by Eqs. (13.155), (13.428), (13.486), and (13.490) is

$$\begin{aligned} E_D\left(^{12}CD\right) &= -\left(14.63489\ eV + 13.603\ eV\right) - E_{T+osc}\left(^{12}CD\right) \\ &= -28.23789\ eV - \left(-31.75462\ eV\right) \\ &= 3.51673\ eV \end{aligned} \tag{13.491}$$

The experimental ^{12}CD bond dissociation energy is [14]

$$E_D\left(^{12}CD\right) = 3.52\ eV \tag{13.492}$$

The results of the determination of bond parameters of CH and CD are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

DIHYDROGEN CARBIDE (CH_2)

The dihydrogen carbide radical CH_2 is formed by the reaction of a hydrogen atom with a hydrogen carbide radical:

$$CH + H \rightarrow CH_2 \tag{13.493}$$

CH_2 can be solved using the same principles as those used to solve H_2O and NH_2 with the exception that the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. Two diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with two carbon $2sp^3$ hybridized orbitals (HOs) to form the MO of CH_2. The solution is very similar to that of CH except that there are two CH bonds in CH_2.

FORCE BALANCE OF CH_2

CH_2 comprises two chemical bonds between carbon and hydrogen atoms. Each $C-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each H-atom electron forms a H_2-type ellipsoidal MO with an unpaired C-atom electrons. However, such a bond is not possible with the outer two C electrons in their ground state since the resulting H_2-type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon $2p$ shell, which is not energetically stable. Thus, when bonding the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422), and (13.428), respectively.

For each $C-H$ bond, a $C2sp^3$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H_2, each of the two $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus. The radius and the energy of the $C2sp^3$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $C-H$ bond is provided by

the spin-pairing force of the CH_2 MO that has the symmetry of an s orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

The energies in the CH_2 MO involve only each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the H_2-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. As in the cases with of OH, H_2O, NH, NH_2, NH_3, and CH the linear combination of each H_2-type ellipsoidal MO with the $C2sp^3$ HO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $C2sp^3$ HO in order to match potential, kinetic, and orbital energy relationships. Thus, the CH_2 MO must comprise two $C-H$ bonds with each comprising 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO:

$$\left[1\ C2sp^3+0.75\ H_2\ MO\right]+\left[1\ C2sp^3+0.75\ H_2\ MO\right]\rightarrow CH_2\ MO \tag{13.494}$$

The force balance of the CH_2 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.494) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH_2 MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the two prolate spheroidal $C-H$-bond MOs comprises a H_2-type-ellipsoidal MO that transitions to the $C2sp^3$ HO, the energy $E\left(C,2sp^3\right)$ in Eq. (13.428) adds to that of the two corresponding H_2-type ellipsoidal MOs to give the total energy of the CH_2 MO. From the energy equation and the relationship between the axes, the dimensions of the CH_2 MO are solved.

The energy components of V_e, V_p, T, and V_m are twice those of CH corresponding to the two $C-H$ bonds. Since the each prolate spheroidal H_2-type MO transitions to the $C2sp^3$ HO and the energy of the $C2sp^3$ shell must remain constant and equal to the $E\left(C,2sp^3\right)$ given by Eq. (13.428), the total energy $E_T\left(CH_2\right)$ of the CH_2 MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C2sp^3$ HO and the two H_2-type ellipsoidal MOs that forms the CH_2 MO as given by Eq. (13.494). Using Eq. (13.431), $E_T\left(CH_2\right)$ is given by

$$\begin{aligned} E_T\left(CH_2\right) &= E_T + E\left(C,2sp^3\right) \\ &= -\frac{e^2}{4\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV \end{aligned} \tag{13.495}$$

The two hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of two H_2-type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the $C2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425). To meet the equipotential condition of the union of the H_2-type-ellipsoidal-MO and the $C2sp^3$ HO, the electron energies in Eq. (13.495) were normalized by the ratio of $14.82575\ eV$, the magnitude of $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each $C-H$-bond MO under the influence of the proton and the C nucleus. Each $C-H$-bond MO comprises the same $C2sp^3$ shell having its energy normalized to that of the Coulombic energy between the electron and a charge of $+e$ at the carbon focus of the CH_2 MO. Thus, the energy of the CH_2 MO is also given by the sum of that of the two H_2-type ellipsoidal MOs given by Eq. (11.212) minus the Coulombic energy, $E_{Coulomb}\left(H\right)=-13.605804\ eV$, of the redundant $+e$ of the linear combination:

$$\begin{aligned} E_T\left(2H_2-H\right) &= -\frac{e^2}{4\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]-E_{Coulomb}\left(H\right) \\ &= 2\left(-31.63536831\ eV\right)-\left(-13.605804\ eV\right) \\ &= -49.66493\ eV \end{aligned} \tag{13.496}$$

$E_T(CH_2)$ given by Eq. (13.495) is set equal to two times the energy of the H_2-type ellipsoidal MO minus the Coulombic energy of H given by Eq. (13.496):

$$E_T(CH_2) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -49.66493\ eV \tag{13.497}$$

From the energy relationship given by Eq. (13.497) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH_2 MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.497) gives

$$\frac{e^2}{4\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e35.03004 \tag{13.498}$$

The most convenient way to solve Eq. (13.498) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.64010a_0 = 8.67903\ X\ 10^{-11}\ m \tag{13.499}$$

Substitution of Eq. (13.499) into Eq. (13.60) gives

$$c' = 1.04566a_0 = 5.53338\ X\ 10^{-11}\ m \tag{13.500}$$

The internuclear distance given by multiplying Eq. (13.500) by two is

$$2c' = 2.09132a_0 = 1.10668\ X\ 10^{-10}\ m \tag{13.501}$$

The experimental bond distance is [38]

$$2c' = 1.111\ X\ 10^{-10}\ m \tag{13.502}$$

Substitution of Eqs. (13.499-13.500) into Eq. (13.62) gives

$$b = c = 1.26354a_0 = 6.68635\ X\ 10^{-11}\ m \tag{13.503}$$

Substitution of Eqs. (13.499-13.500) into Eq. (13.63) gives

$$e = 0.63756 \tag{13.504}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of each H_2-type ellipsoidal MO and the $C2sp^3$ HO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.440-13.448). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{2sp^3} = 0.91771a_0$ is the radius of the $C2sp^3$ shell. Substitution of Eqs. (13.499-13.500) into Eq. (13.261) gives

$$\theta' = 84.54° \tag{13.505}$$

Then, the angle θ_{C2sp^3HO} the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180° - 84.54° = 95.46° \tag{13.506}$$

as shown in Figure 14. The angle θ_{H_2MO} between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the $C2sp^3$ radial vector given by Eqs. (13.442-13.443), (13.503), and (13.506) is

$$\theta_{H_2MO} = 46.30° \tag{13.507}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.499), and (13.507) is

$$d_{H_2MO} = 1.13305a_0 = 5.99585\,X\,10^{-11}\ m \tag{13.508}$$

The distance d_{C2sp^3HO} along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.500), and (13.508) is

$$d_{C2sp^3HO} = 0.08739a_0 = 4.62472\,X\,10^{-12}\ m \tag{13.509}$$

As shown in Eq. (13.494), the uniform charge-density in the $C2sp^3$ HO is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25 for by each $C-H$ bond. Using the orbital composition of CH_2 (Eq. (13.494)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C2sp^3 = 0.91771a_0$ (Eq. (10.424)) shells, and the parameters of the CH_2 MO given by Eqs. (13.3-13.4), (13.499-13.501), and (13.503-13.509), the charge-density of the CH_2 MO comprising the linear combination of two $C-H$-bond MOs is shown in Figure 16. Each $C-H$-bond MO comprises a H_2-type ellipsoidal MO and a $C2sp^3$ HO having the dimensional diagram shown in Figure 14.

ENERGIES OF CH_2

The energies of CH_2 are two times those of CH and are given by the substitution of the semiprincipal axes (Eqs. (13.499-13.500) and (13.503)) into the energy equations Eq. (13.495) and (Eqs. (13.449-13.452)) that are multiplied by two:

$$V_e = (0.91771)\frac{-2e^2}{4\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -72.03287\ eV \quad (13.510)$$

$$V_p = \frac{e^2}{4\pi\varepsilon_0\sqrt{a^2-b^2}} = 26.02344\ eV \quad (13.511)$$

$$T = (0.91771)\frac{\hbar^2}{m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 21.95990\ eV \quad (13.512)$$

$$V_m = (0.91771)\frac{-\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.97995\ eV \quad (13.513)$$

$$E_T(CH_2) = -\frac{e^2}{4\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -49.66437\ eV \quad (13.514)$$

where $E_T(CH_2)$ is given by Eq. (13.495) which is reiteratively matched to Eq. (13.496) within five-significant-figure round-off error.

VIBRATION OF CH_2

The vibrational energy levels of CH_2 may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF $^{12}CH_2$

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of dihydrogen and dideuterium carbide are the same as those of the corresponding hydrogen carbide radicals with the substitution of the dihydrogen and dideuterium carbide parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3 m_e}} = 2.52077\ X\ 10^{16}\ rad/s \quad (13.515)$$

where b is given by Eq. (13.503). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.52077\, X\, 10^{16}\ rad/s = 16.59214\ eV \tag{13.516}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.516) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(16.59214\ eV)}{m_e c^2}} = -0.25493\ eV \tag{13.517}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH_2 due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.517) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having two independent bonds, $\overline{E}'_{osc}\left({}^{12}CH_2\right)$ per bond is

$$\overline{E}'_{osc}\left({}^{12}CH_2\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.518}$$

$$\overline{E}'_{osc}\left({}^{12}CH_2\right) = -0.25493\ eV + \frac{1}{2}(0.35532\ eV) = -0.07727\ eV \tag{13.519}$$

Given that the vibration and reentrant oscillation is for two $C-H$ bonds, $\overline{E}_{osc}\left({}^{12}CH_2\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left({}^{12}CH_2\right) &= 2\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 2\left(-0.25493\ eV + \frac{1}{2}(0.35532\ eV)\right)\\ &= -0.15454\ eV\end{aligned} \tag{13.520}$$

TOTAL AND BOND ENERGIES OF $^{12}CH_2$

$E_{T+osc}\left(^{12}CH_2\right)$, the total energy of the $^{12}CH_2$ radical including the Doppler term, is given by the sum of $E_T\left(CH_2\right)$ (Eq. (13.497)) and $\overline{E}_{osc}\left(^{12}CH_2\right)$ given by Eq. (13.520):

$$\begin{aligned} E_{T+osc}\left(CH_2\right) &= V_e + T + V_m + V_p + E\left(C, 2sp^3\right) + \overline{E}_{osc}\left(^{12}CH_2\right) \\ &= E_T\left(CH_2\right) + \overline{E}_{osc}\left(^{12}CH_2\right) \end{aligned} \tag{13.521}$$

$$\begin{aligned} E_{T+osc}\left(^{12}CH_2\right) &= \left\{ \begin{array}{l} \left(\frac{-e^2}{4\pi\varepsilon_0 c'} \left[(0.91771)\left(2 - \frac{1}{2}\frac{a_0}{a}\right) \ln\frac{a+c'}{a-c'} - 1 \right] - 14.63489\ eV \right) \\ -2\left((31.63536831\ eV) \sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}}{m_e c^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \end{array} \right\} \\ &= -49.66493\ eV - 2\left(0.25493\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \end{aligned} \tag{13.522}$$

From Eqs. (13.518-13.522), the total energy of $^{12}CH_2$ is

$$\begin{aligned} E_{T+osc}\left(^{12}CH_2\right) &= -49.66493\ eV + \overline{E}_{osc}\left(^{12}CH_2\right) \\ &= -49.66493\ eV - 2\left(0.25493\ eV - \frac{1}{2}(0.35532\ eV) \right) \\ &= -49.81948\ eV \end{aligned} \tag{13.523}$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

$^{12}CH_2$ has the same electronic configuration as ^{14}NH. The dissociation of the bond of the dihydrogen carbide radical forms a free hydrogen atom with one unpaired electron and a $C2sp^3$ HO with three unpaired electrons as shown in Eq. (13.422) wherein the magnetic moments cannot all cancel. Thus, the bond dissociation of $^{12}CH_2$ gives rise to ^{12}CH with the same electronic configuration as N as given by Eq. (10.134). The N configuration is more stable than H as shown in Eqs. (10.141-10.143). The lowering of the energy of the reactants decreases the bond energy. The total energy of carbon is reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.424):

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_{2sp^3}\right)^3} = \frac{8\pi\mu_o\mu_B^2}{\left(0.91771a_0\right)^3} = 0.14803\ eV \tag{13.524}$$

The CH_2 bond dissociation energy, $E_D\left({}^{12}CH_2\right)$, is given by the sum of the total energies of the CH radical and the hydrogen atom minus the sum of $E_{T+osc}\left({}^{12}CH_2\right)$ and $E(magnetic)$:

$$E_D\left({}^{12}CH_2\right)=E\left({}^{12}CH\right)+E(H)-E_{T+osc}\left({}^{12}CH_2\right)-E\left(magnetic\right) \tag{13.525}$$

where $E_T({}^{12}CH)$ is given by the sum of the energies of the $C2sp^3$ HO, $E\left(C,2sp^3\right)$ given by Eq. (13.428), $E_D(H)$ given by Eq. (13.154), and the negative of the bond energy of ${}^{12}CH$ given by Eq. (13.489):

$$E({}^{12}CH)=-13.59844\ eV-14.63489\ eV-3.47\ eV=-31.70333\ eV \tag{13.526}$$

Thus, the ${}^{12}CH_2$ bond dissociation energy, $E_D\left({}^{12}CH_2\right)$, given by Eqs. (13.154), and (13.523-13.526) is

$$\begin{aligned}E_D\left({}^{12}CH_2\right)&=-\left(31.70333\ eV+13.59844\ eV\right)-\left(E_{T+osc}\left({}^{12}CH_2\right)+E\left(magnetic\right)\right)\\&=-45.30177\ eV-\left(-49.81948\ eV+0.14803\ eV\right)\\&=4.36968\ eV\end{aligned} \tag{13.527}$$

The experimental ${}^{12}CH_2$ bond dissociation energy is [39]

$$E_D\left({}^{12}CH_2\right)=4.33064\ eV \tag{13.528}$$

BOND ANGLE OF ${}^{12}CH_2$

The CH_2 MO comprises a linear combination of two $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a H_2-type ellipsoidal MO and the $C2sp^3$ HO with a relative charge density of 0.75 to 1.25; otherwise, the $C2sp^3$ shell is unchanged. A bond is also possible between the two H atoms of the $C-H$ bonds. Such $H-H$ bonding would decrease the $C-H$ bond strength since electron density would be shifted from the $C-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $C-H$ bonds is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal H atoms of the $C-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c'=a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}}=\sqrt{\frac{aa_0}{2}} \tag{13.529}$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{13.530}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (13.62).

The bond angle of CH_2 is derived by using the orbital composition and an energy matching factor as in the case with NH_2 and NH_3. Since the two H_2-type ellipsoidal MOs comprise 75% of the H electron density of H_2 and the energy of each H_2-type ellipsoidal MO is matched to that of the $C2sp^3$ HO; the component energies and the total energy E_T of the $H-H$ bond are given by Eqs. (13.67-13.73) except that V_e, T, and V_m are corrected for the hybridization-energy-matching factor of 0.91771 given by Eq. (13.430). Substitution of Eq. (13.529) into Eq. (13.233) with the hybridization factor gives

$$0 = \left[\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left[(0.91771)^{-1}\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1 \right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}} \right] \right.$$
$$\left. +\frac{1}{2}\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o a^3}-\frac{e^2}{8\pi\varepsilon_o (a+c')^3}}{0.5m_p}} \right] \tag{13.531}$$

From the energy relationship given by Eq. (13.531) and the relationship between the axes given by Eqs. (13.529-13.530) and (13.62-13.63), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (13.531) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 5.1500a_0 = 2.7253\,X\,10^{-10}\ m \tag{13.532}$$

Substitution of Eq. (13.532) into Eq. (13.529) gives

$$c' = 1.6047a_0 = 8.4916\,X\,10^{-11}\ m \tag{13.533}$$

The internuclear distance given by multiplying Eq. (13.533) by two is

$$2c' = 3.2094a_0 = 1.6983\,X\,10^{-10}\ m \tag{13.534}$$

Substitution of Eqs. (13.532-13.533) into Eq. (13.62) gives

$$b = c = 4.8936a_0 = 2.5896\,X\,10^{-10}\ m \tag{13.535}$$

Substitution of Eqs. (13.532-13.533) into Eq. (13.63) gives

$$e = 0.3116 \tag{13.536}$$

Using, $2c'_{H-H}$ (Eq. (13.534)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (13.531)), and $2c'_{C-H}$ (Eq. (13.501)), the internuclear distance of each $C-H$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle θ between the $C-H$ bonds is

$$\theta = \cos^{-1}\left(\frac{2(2.09132)^2 - (3.2094)^2}{2(2.09132)^2}\right) = \cos^{-1}(-0.1775) = 100.22^\circ \tag{13.537}$$

The experimental angle between the $C-H$ bonds is [38]

$$\theta = 102.4^\circ \tag{13.538}$$

The results of the determination of bond parameters of CH_2 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

METHYL RADICAL (CH_3)

The methyl radical CH_3 is formed by the reaction of a hydrogen atom with a dihydrogen carbide radical:

$$CH_2 + H \rightarrow CH_3 \tag{13.539}$$

CH_3 can be solved using the same principles as those used to solve and NH_3 with the exception that the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. Three diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with three carbon $2sp^3$ hybridized orbitals (HOs) to form the MO of CH_3. The solution is very similar to that of CH_2 except that there are three CH bonds in CH_3.

FORCE BALANCE OF CH_3

CH_3 comprises three chemical bonds between carbon and hydrogen atoms. Each $C-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each H-atom electron forms a H_2-type ellipsoidal MO with an unpaired C-atom electrons. However, such a bond is not possible with the outer two C electrons in their ground state since the resulting H_2-type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon $2p$ shell which is not energetically stable, and only two electrons are unpaired. Thus, when bonding the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422), and (13.428), respectively.

For each $C-H$ bond, a $C2sp^3$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H_2, each of the three $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus. The radius and the energy of the $C2sp^3$ shell are unchanged with bond formation. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the CH_3 MO that has the symmetry of an s orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

The energies in the CH_3 MO involve only each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the H_2-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. As in the cases with of OH, H_2O, NH, NH_2, NH_3, CH, and CH_2 the linear combination of each H_2-type ellipsoidal MO with the $C2sp^3$ HO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $C2sp^3$ HO in order to match potential, kinetic, and orbital energy relationships. Thus, the CH_3 MO must

comprise three $C-H$ bonds with each comprising 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO:

$$3\left[1\,C2sp^3+0.75\,H_2\,MO\right]\rightarrow CH_3\,MO \tag{13.540}$$

The force balance of the CH_3 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.540) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH_3 MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the three prolate spheroidal $C-H$-bond MOs comprises a H_2-type-ellipsoidal MO that transitions to the $C2sp^3$ HO, the energy $E\left(C,2sp^3\right)$ in Eq. (13.428) adds to that of the three corresponding H_2-type ellipsoidal MOs to give the total energy of the CH_3 MO. From the energy equation and the relationship between the axes, the dimensions of the CH_3 MO are solved.

The energy components of V_e, V_p, T, and V_m are three times those of CH corresponding to the three $C-H$ bonds. Since the each prolate spheroidal H_2-type MO transitions to the $C2sp^3$ HO and the energy of the $C2sp^3$ shell must remain constant and equal to the $E\left(C,2sp^3\right)$ given by Eq. (13.428), the total energy $E_T\left(CH_3\right)$ of the CH_3 MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C2sp^3$ HO and the three H_2-type ellipsoidal MOs that forms the CH_3 MO as given by Eq. (13.540). Using Eq. (13.431), $E_T\left(CH_3\right)$ is given by

$$E_T(CH_3) = E_T + E(C, 2sp^3)$$
$$= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2 - \frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 14.63489\ eV \quad (13.541)$$

The three hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of three H_2-type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the $C2sp^3$ HO-shell Coulombic energy $E_{Coulomb}(C, 2sp^3)$ given by Eq. (13.435). To meet the equipotential condition of the union of the H_2-type-ellipsoidal-MO and the $C2sp^3$ HO, the electron energies in Eqs. (13.431), (13.495), and (13.541) were normalized by the ratio of $14.82575\ eV$, the magnitude of $E_{Coulomb}(C, 2sp^3)$ given by Eq. (13.425), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each $C-H$-bond MO under the influence of the proton and the C nucleus. Each $C-H$-bond MO comprises the same $C2sp^3$ shell having its energy normalized to that of the Coulombic energy between the electron and a charge of $+e$ at the carbon focus of the CH_3 MO. Thus, the energy of the CH_3 MO is also given by the sum of that of the three H_2-type ellipsoidal MOs given by Eq. (11.212) minus two times the Coulombic energy, $E_{Coulomb}(H) = -13.605804\ eV$, of the two redundant $+e$'s of the linear combination:

$$E_T(3H_2 - 2H) = -\frac{3e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2}\right] - 2E_{Coulomb}(H)$$
$$= 3(-31.63536831\ eV) - 2(-13.605804\ eV)$$
$$= -67.69450\ eV$$

(13.542)

$E_T(CH_3)$ given by Eq. (13.541) is set equal to three times the energy of the H_2-type ellipsoidal MO minus two times the Coulombic energy of H given by Eq. (13.542):

$$E_T(CH_3) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2 - \frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] - 14.63489\ eV = -67.69450\ eV$$

(13.543)

From the energy relationship given by Eq. (13.543) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH_3 MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.543) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e53.05961 \tag{13.544}$$

The most convenient way to solve Eq. (13.544) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.62893a_0=8.61990\,X\,10^{-11}\ m \tag{13.545}$$

Substitution of Eq. (13.545) into Eq. (13.60) gives

$$c'=1.04209a_0=5.51450\,X\,10^{-11}\ m \tag{13.546}$$

The internuclear distance given by multiplying Eq. (13.546) by two is

$$2c'=2.08418a_0=1.10290\,X\,10^{-10}\ m \tag{13.547}$$

The experimental bond distance is [38]

$$2c'=1.079\,X\,10^{-10}\ m \tag{13.548}$$

Substitution of Eqs. (13.545-13.546) into Eq. (13.62) gives

$$b=c=1.25198a_0=6.62518\,X\,10^{-11}\ m \tag{13.549}$$

Substitution of Eqs. (13.545-13.546) into Eq. (13.63) gives

$$e=0.63974 \tag{13.550}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of each H_2-type ellipsoidal MO and the $C2sp^3$ HO are given by Eqs. (13.84-13.95), (13.261-13.270), and (13.434-13.442). The polar intersection angle θ' is given by Eq. (13.261) where $r_n=r_{2sp^3}=0.91771a_0$ is the radius of the $C2sp^3$ shell. Substitution of Eqs. (13.545-13.546) into Eq. (13.261) gives

$$\theta'=85.65° \tag{13.551}$$

Then, the angle θ_{C2sp^3HO} the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C2sp^3HO}=180°-85.65°=94.35° \tag{13.552}$$

as shown in Figure 14. The angle θ_{H_2MO} between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the $C2sp^3$ radial vector given by Eqs. (13.442-13.443), (13.549), and (13.552) is

$$\theta_{H_2MO} = 46.96° \tag{13.553}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.545), and (13.553) is

$$d_{H_2MO} = 1.11172a_0 = 5.88295\,X\,10^{-11}\ m \tag{13.554}$$

The distance d_{C2sp^3HO} along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.546), and (13.554) is

$$d_{C2sp^3HO} = 0.06963a_0 = 3.68457\,X\,10^{-12}\ m \tag{13.555}$$

As shown in Eq. (13.540), the uniform charge-density in the $C2sp^3$ HO is increased by a factor of 0.25 and the H-atom density is decreased by a factor of 0.25 for by each $C-H$ bond. Using the orbital composition of CH_3 (Eq. (13.540)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C2sp^3 = 0.91771a_0$ (Eq. (10.424)) shells, and the parameters of the CH_3 MO given by Eqs. (13.3-13.4), (13.545-13.547), and (13.549-13.555), the charge-density of the CH_3 MO comprising the linear combination of three $C-H$-bond MOs is shown in Figure 17. Each $C-H$-bond MO comprises a H_2-type ellipsoidal MO and a $C2sp^3$ HO having the dimensional diagram shown in Figure 14.

ENERGIES OF CH_3

The energies of CH_3 are three times those of CH and are given by the substitution of the semiprincipal axes (Eqs. (13.545-13.546) and (13.549)) into the energy equations Eq. (13.541) and (Eqs. (13.449-13.452)) that are multiplied by three:

$$V_e = 3(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -108.94944\ eV \tag{13.556}$$

$$V_p = \frac{3e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 39.16883\ eV \tag{13.557}$$

$$T = 3(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 33.44213\ eV \tag{13.558}$$

$$V_m = 3(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.72107\ eV \tag{13.559}$$

$$E_T(CH_3) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -67.69444\ eV \tag{13.560}$$

where $E_T(CH_3)$ is given by Eq. (13.541) which is reiteratively matched to Eq. (13.542) within five-significant-figure-round-off-error.

VIBRATION OF CH_3

The vibrational energy levels of CH_3 may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF $^{12}CH_3$

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of methyl radical are the same as those of the corresponding hydrogen carbide radicals with the substitution of the methyl radical parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.55577\,X\,10^{16}\ rad/s \tag{13.561}$$

where b is given by Eq. (13.549). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\bar{E}_K = \hbar\omega = \hbar 2.55577\,X\,10^{16}\ rad/s = 16.82249\ eV \tag{13.562}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic

energy given by Eq. (13.562) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(16.82249\ eV)}{m_e c^2}} = -0.25670\ eV \tag{13.563}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH_3 due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.563) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having three independent bonds, $\overline{E}'_{osc}\left({}^{12}CH_3\right)$ per bond is

$$\overline{E}'_{osc}\left({}^{12}CH_3\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.564}$$

$$\overline{E}'_{osc}\left({}^{12}CH_3\right) = -0.25670\ eV + \frac{1}{2}(0.35532\ eV) = -0.07904\ eV \tag{13.565}$$

Given that the vibration and reentrant oscillation is for three $C-H$ bonds, $\overline{E}_{osc}\left({}^{12}CH_3\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left({}^{12}CH_3\right) &= 3\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 3\left(-0.25670\ eV + \frac{1}{2}(0.35532\ eV)\right)\\ &= -0.23711\ eV\end{aligned} \tag{13.566}$$

TOTAL AND BOND ENERGIES OF ${}^{12}CH_3$

$E_{T+osc}\left({}^{12}CH_3\right)$, the total energy of the ${}^{12}CH_3$ radical including the Doppler term, is given by the sum of $E_T(CH_3)$ (Eq. (13.543)) and $\overline{E}_{osc}\left({}^{12}CH_3\right)$ given by Eq. (13.566):

$$\begin{aligned}E_{T+osc}(CH_3) &= V_e + T + V_m + V_p + E\left(C, 2sp^3\right) + \overline{E}_{osc}\left({}^{12}CH_3\right)\\ &= E_T(CH_3) + \overline{E}_{osc}\left({}^{12}CH_3\right)\end{aligned} \tag{13.567}$$

$$E_{T+osc}\left({}^{12}CH_3\right)=\left\{\begin{array}{l}\left(\frac{-3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV\right)\\ -3\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}}{m_e c^2}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\} \quad (13.568)$$

$$=-67.69450\ eV-3\left(0.25670\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

From Eqs. (13.564-13.568), the total energy of ${}^{12}CH_3$ is

$$\begin{aligned}E_{T+osc}\left({}^{12}CH_3\right)&=-67.69450\ eV+\bar{E}_{osc}\left({}^{12}CH_3\right)\\&=-67.69450\ eV-3\left(0.25670\ eV-\frac{1}{2}(0.35532\ eV)\right)\\&=-67.93160\ eV\end{aligned} \quad (13.569)$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The CH_3 bond dissociation energy, $E_D\left({}^{12}CH_3\right)$, is given by the sum of the total energies of the CH_2 radical and the hydrogen atom minus $E_{T+osc}\left({}^{12}CH_3\right)$:

$$E_D\left({}^{12}CH_3\right)=E\left({}^{12}CH_2\right)+E(H)-E_{T+osc}\left({}^{12}CH_3\right) \quad (13.570)$$

where $E_T({}^{12}CH_2)$ is given by the sum of the energies of the $C2sp^3$ HO, $E\left(C,2sp^3\right)$ given by Eq. (13.428), $2E_D(H)$ given by Eq. (13.154), and the negative of the bond energies of ${}^{12}CH$ given by Eq. (13.489) and ${}^{12}CH_2$ given by Eq. (13.528):

$$E({}^{12}CH_2)=2(-13.59844\ eV)-14.63489\ eV-3.47\ eV-4.33064\ eV=-49.63241\ eV \quad (13.571)$$

Thus, the ${}^{12}CH_3$ bond dissociation energy, $E_D\left({}^{12}CH_3\right)$, given by Eqs. (13.154), and (13.569-13.571) is

$$\begin{aligned}E_D\left({}^{12}CH_3\right)&=-(-49.63241\ \ eV-13.59844\ eV)-E_{T+osc}\left({}^{12}CH_3\right)\\&=-63.23085eV-(-67.93160\ eV)\\&=4.70075\ eV\end{aligned} \quad (13.572)$$

The experimental ${}^{12}CH_3$ bond dissociation energy is [40]

$$E_D\left({}^{12}CH_3\right)=4.72444\ eV \quad (13.573)$$

BOND ANGLE OF $^{12}CH_3$

Using, $2c'_{H-H}$ (Eq. (13.534)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (13.531)), and $2c'_{C-H}$, the internuclear distance of each $C-H$ bond (Eq. (13.547)), the corresponding bond angle can be determined from the law of cosines. Using Eq. (13.537), the bond angle θ between the $C-H$ bonds is

$$\begin{aligned}\theta &= \cos^{-1}\left(\frac{2(2.08418)^2-(3.2094)^2}{2(2.08418)^2}\right)\\ &= \cos^{-1}(-0.18560)\\ &= 100.70^\circ\end{aligned} \tag{13.574}$$

The CH_3 radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance $d_{origin-H}$ from the origin to the nucleus of a hydrogen atom given by Eqs. (13.534) and (13.412) is

$$d_{origin-H} = 1.85293a_0 \tag{13.575}$$

The height along the z-axis of the pyramid from the origin to C nucleus d_{height} given by Eqs. (13.414), (13.547), and (13.575) is

$$d_{height} = 0.95418a_0 \tag{13.576}$$

The angle θ_v of each $C-H$ bond from the z-axis given by Eqs. (13.416), (13.575), and (13.576) is

$$\theta_v = 62.75^\circ \tag{13.577}$$

The CH_3 MO shown in Figure 17 was rendered using these parameters.

The results of the determination of bond parameters of CH_3 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

METHANE MOLECULE (CH_4)

The methane molecule CH_4 is formed by the reaction of a hydrogen atom with a methyl radical:

$$CH_3 + H \rightarrow CH_4 \tag{13.578}$$

CH_4 can be solved using the same principles as those used to solve and CH_3 wherein the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. Four diatomic molecular orbitals (MOs) developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section serve as basis functions in a linear combination with four carbon $2sp^3$ hybridized orbitals (HOs) to form the MO of CH_4. The solution is very similar to that of CH_3 except that there are four CH bonds in CH_4. Methane is the simplest hydrocarbon that can be solved using the results for CH_3. From the solution of CH_2 as well as CH_3, more complex hydrocarbons can be solved using these radical as basis elements with bonding between the $C2sp^3$ hybridized carbons.

FORCE BALANCE OF CH_4

CH_4 comprises four chemical bonds between carbon and hydrogen atoms. Each $C-H$ bond comprises two spin-paired electrons with one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom. Each H-atom electron forms a H_2-type ellipsoidal MO with an unpaired C-atom electrons. However, such a bond is not possible with the outer two C electrons in their ground state since the resulting H_2-type ellipsoidal MO would have a shorter internuclear distance than the radius of the carbon $2p$ shell which is not energetically stable, and only two electrons are unpaired. Thus, when bonding the carbon $2s$ and $2p$ shells hybridize to form a single $2sp^3$ shell as an energy minimum. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422), and (13.428), respectively.

For each $C-H$ bond, a $C2sp^3$ electron combines with the $H1s$ electron to form a molecular orbital. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H_2, each of the four $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that can be solve as being continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus. The radius and the energy of the $C2sp^3$ shell are

unchanged with bond formation. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the CH_4 MO that has the symmetry of an s orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

The energies in the CH_4 MO involve only each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the H_2-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. As in the cases with of OH, H_2O, NH, NH_2, NH_3, CH, CH_2, and CH_3 the CH_4, the CH_4 MO must comprise four $C-H$ bonds with each having 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO in a linear combination in order to match potential, kinetic, and orbital energy relationships:

$$4\left[1\,C2sp^3+0.75\,H_2\;MO\right]\rightarrow CH_4\;MO \tag{13.579}$$

The force balance of the CH_4 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.579) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH_4 MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the four prolate spheroidal $C-H$-bond MOs comprises a H_2-type-ellipsoidal MO that transitions to the $C2sp^3$ HO, the energy $E\left(C,2sp^3\right)$ in Eq. (13.428) adds to that of the four corresponding H_2-type ellipsoidal MOs to give the total energy of the CH_4 MO. From the energy equation and the relationship between the axes, the dimensions of the CH_4 MO are solved.

The energy components of V_e, V_p, T, and V_m are four times those of CH corresponding to the four $C-H$ bonds. Since the each prolate spheroidal H_2-type MO transitions to the $C2sp^3$ HO and the energy of the $C2sp^3$ shell must remain constant and equal to the $E\left(C,2sp^3\right)$ given by Eq. (13.428), the total energy $E_T\left(CH_4\right)$ of the CH_4 MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C2sp^3$ HO and the four H_2-type ellipsoidal MOs that forms the CH_4 MO as given by Eq. (13.579). Using Eq. (13.431), $E_T\left(CH_4\right)$ is given by

$$\begin{aligned} E_T\left(CH_4\right) &= E_T + E\left(C,2sp^3\right) \\ &= -\frac{4e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV \end{aligned} \tag{13.580}$$

The four hydrogen atoms and the hybridized carbon atom can achieve an energy minimum as a linear combination of four H_2-type ellipsoidal MOs each having the proton and the carbon nucleus as the foci. Hybridization gives rise to the $C2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.435). To meet the equipotential condition of the union of the H_2-type-ellipsoidal-MO and the $C2sp^3$ HO, the electron energies in Eqs. (13.431), (13.495), (13.541), and (13.580) were normalized by the ratio of $14.82575\ eV$, the magnitude of $E_{Coulomb}\left(C,2sp^3\right)$ given by Eq. (13.425), and $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The factor given by Eq. (13.430) normalized the energies to match that of the Coulombic energy alone to meet the energy matching condition of each $C-H$-bond MO under the influence of the proton and the C nucleus. Each $C-H$-bond MO comprises the same $C2sp^3$ shell having its energy normalized to that of the Coulombic energy between the electron and a charge of $+e$ at the carbon focus of the CH_4 MO. Thus, the energy of the CH_4 MO is also given by the sum of that of the four H_2-type ellipsoidal MOs given by Eq. (11.212) minus three times the Coulombic energy, $E_{Coulomb}\left(H\right)=-13.605804\ eV$, of the three redundant $+e$'s of the linear combination:

$$E_T(4H_2-3H)=-\frac{4e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]-3E_{Coulomb}(H)$$
$$=4(-31.63536831\ eV)-3(-13.605804\ eV) \quad (13.581)$$
$$=-85.72406\ eV$$

$E_T(CH_4)$ given by Eq. (13.580) is set equal to four times the energy of the H_2-type ellipsoidal MO minus three times the Coulombic energy of H given by Eq. (13.581):

$$E_T(CH_4)=-\frac{4e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV=-85.72406\ eV \quad (13.582)$$

From the energy relationship given by Eq. (13.582) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH_4 MO can be solved.

Substitution of Eq. (13.60) into Eq. (13.543) gives

$$\frac{4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e71.08917 \quad (13.583)$$

The most convenient way to solve Eq. (13.583) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.62340a_0=8.59066\,X\,10^{-11}\ m \quad (13.584)$$

Substitution of Eq. (13.584) into Eq. (13.60) gives

$$c'=1.04032a_0=5.50514\,X\,10^{-11}\ m \quad (13.585)$$

The internuclear distance given by multiplying Eq. (13.585) by two is

$$2c'=2.08064a_0=1.10103\,X\,10^{-10}\ m \quad (13.586)$$

The experimental bond distance is [41]

$$2c'=1.087\,X\,10^{-10}\ m \quad (13.587)$$

Substitution of Eqs. (13.584-13.585) into Eq. (13.62) gives

$$b=c=1.24626a_0=6.59492\,X\,10^{-11}\ m \quad (13.588)$$

Substitution of Eqs. (13.584-13.585) into Eq. (13.63) gives

$$e=0.64083 \quad (13.589)$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of each H_2-type ellipsoidal

MO and the $C2sp^3$ HO in the absence of the other three are given by Eqs. (13.84-13.95), (13.261-13.270), (13.434-13.442), and (13.551-13.555). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{2sp^3} = 0.91771a_0$ is the radius of the $C2sp^3$ shell. Substitution of Eqs. (13.584-13.585) into Eq. (13.261) gives

$$\theta' = 86.20° \tag{13.590}$$

Then, the angle θ_{C2sp^3HO} the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C2sp^3HO} = 180° - 86.20° = 93.80° \tag{13.591}$$

as shown in Figure 14. The angle θ_{H_2MO} between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the $C2sp^3$ radial vector given by Eqs. (13.442-13.443), (13.588), and (13.591) is

$$\theta_{H_2MO} = 47.29° \tag{13.592}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals given by Eqs. (13.445), (13.584), and (13.592) is

$$d_{H_2MO} = 1.10121a_0 = 5.82734\,X\,10^{-11}\ m \tag{13.593}$$

The distance d_{C2sp^3HO} along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals given by Eqs. (13.447), (13.585), and (13.593) is

$$d_{C2sp^3HO} = 0.06089a_0 = 3.22208\,X\,10^{-12}\ m \tag{13.594}$$

The H_2-type ellipsoidal MOs do not actually directly contact the $C2sp^3$ HO. As discussed in the Force Balance of H_2O section, with the addition of the fourth $C-H$ bond, the H_2-type ellipsoidal MOs may linearly combine to form a continuous two-dimensional surface of equipotential equivalent to that of the MOs if they did contact the $C2sp^3$ HO. However, Eqs. (13.579-13.580) must hold based on conservation of momentum and the potential, kinetic, and total energy relationships. In order that there is current continuity given the constraints of Eqs. (13.579-13.580), the existence of a self-contained, continuous-current, linear-combination of the H_2-type ellipsoidal MOs requires that electrons are divisible between the combination H_2-type MO and the $C2sp^3$ HO. This is not possible. Thus, at the points of intersection of the H_2-type MOs of methane, symmetry, electron

indivisibility, current continuity, and conservation of energy and angular momentum require that the current between the $C2sp^3$ shell and points of mutual contact is projected onto and flows along the radial vector to the surface of $C2sp^3$ shell. This current designated the bisector current (BC) meets the $C2sp^3$ surface and does not travel to distances shorter than its radius. Moreover, an energy minimum is obtained when the H-atom charge-density of each $C-H$-bond MO is decreased by a factor of 0.25 with a corresponding 0.25 increase in that of the three other $C-H$-bond MOs. In this case, the angular momentum components of the transferred current mutually cancel. The geometry of the equivalent bonds is tetrahedral. The symmetry point group is T_d. This geometry is equivalent to the indistinguishable bonds positioned uniformly on a spherical surface or also at the apexes of a cube. The predicted angle θ between the $C-H$ bonds is

$$\theta = 109.5° \tag{13.595}$$

The experimental bond angle is [41]

$$\theta = 109.5° \tag{13.596}$$

The polar angle ϕ at which the H_2-type ellipsoidal MOs intersect is given by the bisector of the angle θ between the $C-H$ bonds:

$$\phi = \frac{109.5}{2} = 54.75° \tag{13.597}$$

With the carbon nucleus defined as the origin and one of the $C-H$ bonds defined as the positive x-axis, the polar-coordinate angle of the intersection occurs at

$$\phi' = 54.75° + 180° = 234.57° \tag{13.598}$$

The polar radius r_i at this angle is given by Eqs. (13.84-13.85):

$$r_i = (a-c')\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\phi'} \tag{13.599}$$

Substitution of Eqs. (13.584-13.585) and (13.589) into Eq. (13.599) gives

$$r_i = 1.52223a_0 = 8.05530\,X\,10^{-11}\,m \tag{13.600}$$

Using the orbital composition of CH_4 (Eq. (13.579)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C2sp^3 = 0.91771a_0$ (Eq. (10.424)) shells, and the parameters of the CH_4 MO given by Eqs. (13.3-13.4), (13.584-13.586), and (13.588-13.600), the charge-density of the CH_4 MO comprising the linear combination of four $C-H$-bond MOs is shown in

Figure 18. Each $C-H$-bond MO having the dimensional diagram shown in Figure 14 comprises a H_2-type ellipsoidal MO and a $C2sp^3$ HO according to Eq. (13.579). But, based on the T_d symmetry of the H_2-type MOs, the charge is distributed 1:1 between the H_2-type MOs and the $C2sp^3$ shell.

ENERGIES OF CH_4

The energies of CH_4 are four times those of CH and are given by the substitution of the semiprincipal axes (Eqs. (13.584-13.585) and (13.588)) into the energy equations Eq. (13.580) and (Eqs. (13.449-13.452)) that are multiplied by four:

$$V_e = 4(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -145.86691\ eV \tag{13.601}$$

$$V_p = \frac{4e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 52.31390\ eV \tag{13.602}$$

$$T = 4(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 44.92637\ eV \tag{13.603}$$

$$V_m = 4(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -22.46318\ eV \tag{13.604}$$

$$E_T(CH_4) = -\frac{4e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV = -85.72472\ eV \tag{13.605}$$

where $E_T(CH_4)$ is given by Eq. (13.580) which is reiteratively matched to Eq. (13.581) within five-significant-figure round-off error.

VIBRATION OF CH_4

The vibrational energy levels of CH_4 may be solved as four equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [2] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF $^{12}CH_4$

The reentrant oscillation of hybridized orbitals in the transition state is not coupled. Therefore, the equations of the radiation reaction force of methane are the same as those of OH, CH, CH_2, and CH_3 with the substitution of the methane parameters. Using Eqs. (11.136) and (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}} = 2.57338\ X\ 10^{16}\ rad/s \tag{13.606}$$

where b is given by Eq. (13.588). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.57338\ X\ 10^{16}\ rad/s = 16.93841\ eV \tag{13.607}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.607) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the four bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(16.93841\ eV)}{m_e c^2}} = -0.25758\ eV \tag{13.608}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH_4 due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.608) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having four independent bonds, $\overline{E}'_{osc}(^{12}CH_4)$ per bond is

$$\overline{E}'_{osc}(^{12}CH_4) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.609}$$

$$\overline{E}'_{osc}(^{12}CH_4) = -0.25758\ eV + \frac{1}{2}(0.35532\ eV) = -0.07992\ eV \tag{13.610}$$

The reentrant orbit for the binding of a hydrogen atom to a CH_3 radical involves four $C-H$ bonds. Since the vibration and reentrant oscillation is along four bonds, $\overline{E}_{osc}$ for $^{12}CH_4$, $\overline{E}_{osc}\left(^{12}CH_4\right)$, is:

$$\begin{aligned}\overline{E}_{osc}\left(^{12}CH_4\right) &= 4\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \\ &= 4\left(-0.25758\ eV + \frac{1}{2}(0.35532\ eV)\right) \\ &= -0.31967\ eV\end{aligned} \tag{13.611}$$

TOTAL AND BOND ENERGIES OF $^{12}CH_4$

$E_{T+osc}\left(^{12}CH_4\right)$, the total energy of the $^{12}CH_4$ radical including the Doppler term, is given by the sum of $E_T\left(CH_4\right)$ (Eq. (13.582)) and $\overline{E}_{osc}\left(^{12}CH_4\right)$ given by Eq. (13.611):

$$\begin{aligned}E_{T+osc}\left(CH_4\right) &= V_e + T + V_m + V_p + E\left(C, 2sp^3\right) + \overline{E}_{osc}\left(^{12}CH_4\right) \\ &= E_T\left(CH_4\right) + \overline{E}_{osc}\left(^{12}CH_4\right)\end{aligned} \tag{13.612}$$

$$\begin{aligned}E_{T+osc}\left(^{12}CH_4\right) &= \left\{\begin{array}{l}\left(\frac{-4e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.63489\ eV\right) \\ -4\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}}{m_e}}{m_e c^2}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\} \\ &= -85.72406\ eV - 4\left(0.25758\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned}$$

(13.613)

From Eqs. (13.609-13.613), the total energy of $^{12}CH_4$ is

$$\begin{aligned}E_{T+osc}\left(^{12}CH_4\right) &= -85.72406\ eV + \overline{E}_{osc}\left(^{12}CH_4\right) \\ &= -85.72406\ eV - 4\left(0.25758\ eV - \frac{1}{2}(0.35532\ eV)\right) \\ &= -86.04373\ eV\end{aligned} \tag{13.614}$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The CH_4 bond dissociation energy, $E_D\left({}^{12}CH_4\right)$, is given by the sum of the total energies of the CH_3 radical and the hydrogen atom minus $E_{T+osc}\left({}^{12}CH_4\right)$:

$$E_D\left({}^{12}CH_4\right)=E\left({}^{12}CH_3\right)+E(H)-E_{T+osc}\left({}^{12}CH_4\right) \tag{13.615}$$

where $E_T({}^{12}CH_3)$ is given by the sum of the energies of the $C2sp^3$ HO, $E\left(C,2sp^3\right)$ given by Eq. (13.428), $3E_D(H)$ given by Eq. (13.154), and the negative of the bond energies of ${}^{12}CH$ given by Eq. (13.489), ${}^{12}CH_2$ given by Eq. (13.528), and ${}^{12}CH_3$ given by Eq. (13.573):

$$E({}^{12}CH_3)=\begin{pmatrix}3(-13.59844\ eV)-14.63489\ eV\\-3.47\ eV-4.33064\ eV-4.72444\ eV\end{pmatrix}=-67.95529\ eV \tag{13.616}$$

Thus, the ${}^{12}CH_4$ bond dissociation energy, $E_D\left({}^{12}CH_4\right)$, given by Eqs. (13.154), and (13.614-13.616) is

$$\begin{aligned}E_D\left({}^{12}CH_4\right)&=-(67.95529\ eV+13.59844\ eV)-E_{T+osc}\left({}^{12}CH_4\right)\\&=-81.55373\ eV-(-86.04373\ eV)\\&=4.4900\ eV\end{aligned} \tag{13.617}$$

The experimental ${}^{12}CH_4$ bond dissociation energy is [40]

$$E_D\left({}^{12}CH_4\right)=4.48464\ eV \tag{13.618}$$

The results of the determination of bond parameters of CH_4 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

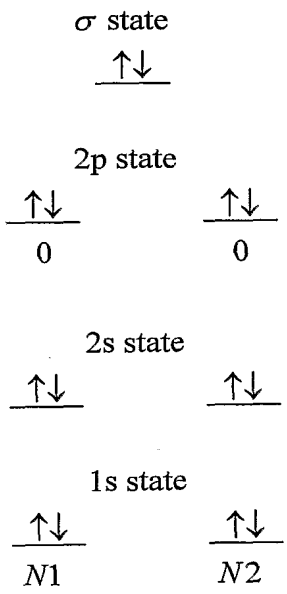
NITROGEN MOLECULE

The nitrogen molecule can be formed by the reaction of two nitrogen atoms:

$$N+N\rightarrow N_2 \tag{13.619}$$

The bond in the nitrogen molecule comprises a H_2-type molecular orbital (MO) with two paired electrons. The force balance equation and radius r_7 of the $2p$ shell of N is derived in the Seven-Electron Atoms section. With the formation of the H_2-type MO by the contribution of a $2p$ electron from each N atom, a diamagnetic force arises between the

remaining $2p$ electrons and the H_2-type MO. This force from each N causes the H_2-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $2p$ electrons of each N decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of N_2 is $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^2 2p_2^2 \sigma_{1,2}^2$ where the subscript designates the N atom, 1 or 2, σ designates the H_2-type MO, and the orbital arrangement is



(13.620)

Nitrogen is predicted to be diamagnetic in agreement with observations [42].

FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOMS OF THE NITROGEN MOLECULE

For each N atom, force balance for the outermost $2p$ electron of N_2 (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$-shell as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of N_2 (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with

the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i}_r \tag{13.621}$$

for $r > r_5$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contribution is the same as that of the reactant nitrogen atoms given by Eq. (10.136) with r_6 replacing r_7:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{13.622}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved orbital angular momentum of the three orbitals is given by Eq. (10.89):

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.623}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{13.624}$$

In addition, the contribution of a $2p$ electron from each N atom in the formation of the σ MO gives rise to a paramagnetic force on the remaining two $2p$ electrons that pair. The force, $\mathbf{F}_{mag\ 3}$, follows from Eq. (10.11) wherein the two radii are equal to r_6 and the direction is positive, central:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.625}$$

$\mathbf{F}_{mag\ 3}$ is present in additional diatomic molecules where its contribution minimizes the energy. This AO spin-pairing force reduces the radius directly to reduce the energy, and it can also cancel the contribution of the corresponding electron to $\mathbf{F}_{diamagnetic}$ to further reduce the energy.

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.621)) and diamagnetic (Eqs. (13.622) and (13.624)), and paramagnetic (Eqs. (13.623) and (13.625)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left(\begin{array}{l} \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12 m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{3\hbar^2}{Z m_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4 m_e r_6^3}\sqrt{s(s+1)} \end{array} \right) \tag{13.626}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (13.626) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4 m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12 m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Z m_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.627}$$

The quadratic equation corresponding to Eq. (13.627) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.628}$$

The solution of Eq. (13.628) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-5)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2} \tag{13.629}$$

r_3 *in units of* a_0

The positive root of Eq. (13.629) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (13.629) gives

$$r_6 = 0.78402 a_0 \tag{13.630}$$

ENERGIES OF THE $2p$ SHELL OF THE NITROGEN ATOMS OF THE NITROGEN MOLECULE

The central forces on the $2p$ shell of each N are increased with the formation of the σ MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two N atoms at the new radius are calculated and added to the energy of the σ MO to give the total energy of N_2. Then, the bond energy is determined from the total N_2 energy.

The radius r_7 of each nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084a_0 \tag{13.631}$$

Using the initial radius r_7 of each N atom and the final radius r_6 of the $N2p$ shell of N_2 (Eq. (13.630)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(N_2,2p)$ of the Coulombic energy change of the $N2p$ electrons of both atoms is determined using Eq. (10.102):

$$\begin{aligned} E_T(N_2,2p) &= -2\sum_{n=4}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_7}\right) \\ &= -2(13.60580\ eV)(0.20118)(2+3) \\ &= -27.37174\ eV \end{aligned} \tag{13.632}$$

FORCE BALANCE OF THE σ MO OF THE NITROGEN MOLECULE

The $2p$ shell gives rise to two diamagnetic forces on the σ MO. As given for the hydrogen molecule in the Hydrogen-Type Molecules section, the σ MO comprises two electrons, σ electron 1 and σ electron 2, that are bound at $\xi = 0$ as a equipotential prolate spheroidal MO by the central Coulombic field due to the nitrogen atoms at the foci and the spin pairing force on σ electron 2 due to σ electron 1 that initially has smaller semiprincipal axes. The spin-pairing force given in Eq. (11.200) is equal to one half the centrifugal force of the two electrons. The spin-pairing electron of the σ MO is also repelled by the remaining $2p$ electrons of each N according to Lenz law, and the force is based on the total number of these electrons n_e that interact with the binding σ-MO electron. This diamagnetic force $\mathbf{F}_{diamagneticMO1}$ is of the same form as the molecular spin-pairing force but in the opposite direction. The force follows from the derivations of Eqs. (10.219) and (11.200) which gives:

$$\mathbf{F}_{diamagneticMO1} = \frac{n_e \hbar^2}{4 m_e a^2 b^2} D \mathbf{i}_\xi \tag{13.633}$$

In addition, there is a relativistically corrected Lorentzian force $\mathbf{F}_{diamagneticMO2}$ on the pairing electron of the σ MO that follows from Eqs. (7.15) and (11.200):

$$\mathbf{F}_{diamagneticMO2} = \frac{1}{Z} \frac{|L| \hbar}{2 m_e a^2 b^2} D \mathbf{i}_\xi \tag{13.634}$$

where $|L|$ is the magnitude of the angular momentum of each N atom at a focus that is the source of the diamagnetism at the σ-MO.

The force balance equation for the σ-MO of the nitrogen molecule given by Eq. (11.200) and Eqs. (13.633-13.634) with $n_e = 2$ and $|L| = \hbar$ is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8 \pi \varepsilon_0 a b^2} D + \frac{\hbar^2}{2 m_e a^2 b^2} D - \left(1 + \frac{1}{Z}\right) \frac{\hbar^2}{2 m_e a^2 b^2} D \tag{13.635}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8 \pi \varepsilon_0 a b^2} D - \frac{1}{Z} \frac{\hbar^2}{2 m_e a^2 b^2} D \tag{13.636}$$

$$\left(2 + \frac{1}{Z}\right) \frac{\hbar^2}{2 m_e a^2 b^2} D = \frac{e^2}{8 \pi \varepsilon_0 a b^2} D \tag{13.637}$$

$$a = \left(2 + \frac{1}{Z}\right) a_0 \tag{13.638}$$

Substitution of $Z = 7$ into Eq. (13.638) gives

$$a = 2.14286 a_0 = 1.13395 \, X \, 10^{-10} \, m \tag{13.639}$$

Substitution of Eq. (13.639) into Eq. (11.79) is

$$c' = 1.03510 a_0 = 5.47750 \, X \, 10^{-11} \, m \tag{13.640}$$

The internuclear distance given by multiplying Eq. (13.640) by two is

$$2c' = 2.07020 a_0 = 1.09550 \, X \, 10^{-10} \, m \tag{13.641}$$

The experimental bond distance from Ref. [28] and Ref. [43] is

$$2c' = 1.09769 \, X \, 10^{-10} \, m \tag{13.642}$$

$$2c' = 1.094 \, X \, 10^{-10} \, m \tag{13.643}$$

Substitution of Eqs. (13.639-13.640) into Eq. (11.80) is

$$b = c = 1.87628 a_0 = 9.92882 \, X \, 10^{-11} \, m \tag{13.644}$$

Substitution of Eqs. (13.639-13.640) into Eq. (11.67) is

$$e = 0.48305 \tag{13.645}$$

Using the electron configuration of N_2 (Eq. (13.620)), the radii of the $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), and $N2p = 0.78402a_0$ (Eq. (13.630)) shells and the parameters of the σ MO of N_2 given by Eqs. (13.3-13.4), (13.639-13.641), and (13.644-13.645), the dimensional diagram and charge-density of the N_2 MO are shown in Figures 19 and 20, respectively.

Despite the predictions of standard quantum mechanics that preclude the imaging of a molecular orbital, the full three-dimensional structure of the outer molecular orbital of N_2 has been recently tomographically reconstructed [44]. The charge-density surface observed is consistent with that shown in Figure 20. This result constitutes direct evidence that electrons are not point-particle probability waves that have no form until they are "collapsed to a point" by measurement. Rather they are physical, two-dimensional equipotential charge density surfaces.

SUM OF THE ENERGIES OF THE σ MO AND THE AOs OF THE NITROGEN MOLECULE

The energies of the N_2 σ MO are given by the substitution of the semiprincipal axes (Eqs. (13.639-13.640) and (13.644)) into the energy equations (Eqs. (11.207-11.212)) of H_2:

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -27.70586\ eV \tag{13.646}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 13.14446\ eV \tag{13.647}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 6.46470\ eV \tag{13.648}$$

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -3.23235\ eV \tag{13.649}$$

$$E_T = V_e + T + V_m + V_p \tag{13.650}$$

Substitution of Eqs. (11.79) and (13.646-13.649) into Eq. (13.650) gives

$$E_T(N_2,\sigma) = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right) = -11.32906\ eV \tag{13.651}$$

where $E_T(N_2,\sigma)$ is the total energy of the σ MO of N_2. The sum, $E_T(N_2)$, of $E_T(N_2,2p)$, the $2p$ (AO) contribution given by Eq. (13.632), and $E_T(N_2,\sigma)$, the σ MO contribution given by Eq. (13.651) is:

$$\begin{aligned} E_T(N_2) &= E_T(N_2,2p)+E_T(N_2,\sigma) \\ &= -27.37174\ eV - 11.32906\ eV \\ &= -38.70080\ eV \end{aligned} \tag{13.652}$$

VIBRATION OF N_2

The vibrational energy levels of N_2 may be solved by determining the Morse potential curve from the energy relationships for the transition from two N atoms whose parameters are given by Eqs. (10.134-10.143) to the two N atoms whose parameter r_6 is given by Eq. (13.630) and the σ MO whose parameters are given by Eqs. (13.639-13.641) and (13.644-13.645). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF THE NITROGEN MOLECULE

The equations of the radiation reaction force of nitrogen are the same as those of H_2 with the substitution of the nitrogen parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 1.31794\ X\ 10^{16}\ rad/s \tag{13.653}$$

where a is given by Eq. (13.639). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 1.31794\ X\ 10^{16}\ rad/s = 8.67490\ eV \tag{13.654}$$

In Eq. (11.181), substitution of $E_T(N_2)$ for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.654) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -38.70080\ eV\sqrt{\frac{2e(8.67490\ eV)}{m_e c^2}} = -0.22550\ eV \tag{13.655}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the N_2 MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.655) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental N_2 ω_e of 2358.57 cm^{-1} (0.29243 eV) [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(N_2)$ is

$$\overline{E}_{osc}(N_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.656}$$

$$\overline{E}_{osc}(N_2) = -0.22550\ eV + \frac{1}{2}(0.29243\ eV) = -0.07929\ eV \tag{13.657}$$

TOTAL AND BOND ENERGIES OF THE NITROGEN MOLECULE

$E_{T+osc}(N_2)$, the total energy of N_2 including the Doppler term, is given by the sum of $E_T(N_2)$ (Eq. (13.652)) and $\overline{E}_{osc}(N_2)$ given by Eq. (13.657):

$$\begin{aligned} E_{T+osc}(N_2) &= V_e + T + V_m + V_p + E_T(N_2, 2p) + \overline{E}_{osc}(N_2) \\ &= E_T(N_2, \sigma) + E_T(N_2, 2p) + \overline{E}_{osc}(N_2) \\ &= E_T(N_2) + \overline{E}_{osc}(N_2) \end{aligned} \tag{13.658}$$

$$E_{T+osc}(N_2)=\left\{\begin{array}{l}\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right)-2\sum_{n=4}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_7}\right)\right)\\ \left(1+\sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right)+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\end{array}\right\} \quad (13.659)$$

$$=-38.70080\ eV-0.22550\ eV+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

From Eqs. (13.656-13.659), the total energy of the N_2 MO is

$$\begin{aligned}E_{T+osc}(N_2)&=-38.70080\ eV+\bar{E}_{osc}(N_2)\\&=-38.70080\ eV-0.22550\ eV+\frac{1}{2}(0.29243\ eV)\\&=-38.78009\ eV\end{aligned} \quad (13.660)$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The N_2 bond dissociation energy, $E_D(N_2)$, is given by the difference in the total energies of the two N atoms and $E_{T+osc}(N_2)$:

$$E_D(N_2)=2E(N)-E_{T+osc}(N_2) \quad (13.661)$$

where the energy of a nitrogen atom is [6]

$$E(N)=-14.53414\ eV \quad (13.662)$$

Thus, the N_2 bond dissociation energy, $E_D(N_2)$, given by Eqs. (13.660-13.662) is

$$\begin{aligned}E_D(N_2)&=-2(14.53414\ eV)-E_{T+osc}(N_2)\\&=-29.06828\ eV-(-38.78009\ eV)\\&=9.71181\ eV\end{aligned} \quad (13.663)$$

The experimental N_2 bond dissociation energy from Ref. [43] and Ref. [45] is

$$E_D(N_2)=9.756\ eV \quad (13.664)$$

$$E_D(N_2)=9.764\ eV \quad (13.665)$$

The results of the determination of bond parameters of N_2 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations

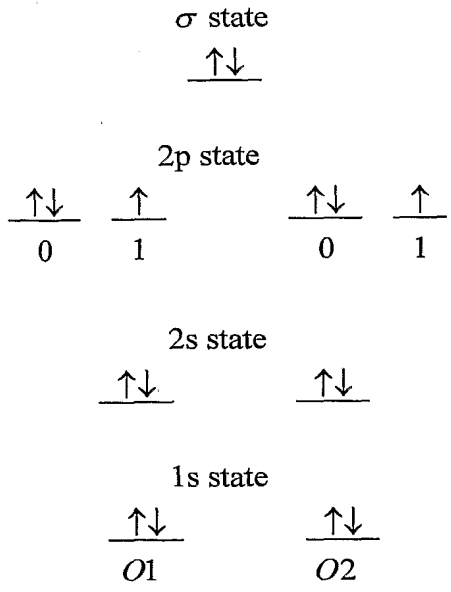
containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

OXYGEN MOLECULE

The oxygen molecule can be formed by the reaction of two oxygen atoms:

$$O+O \rightarrow O_2 \tag{13.666}$$

The bond in the oxygen molecule comprises a H_2-type molecular orbital (MO) with two paired electrons. The force balance equation and radius r_8 of the $2p$ shell of O is derived in the Eight-Electron Atoms section. With the formation of the H_2-type MO by the contribution of a $2p$ electron from each O atom, a diamagnetic force arises between the remaining $2p$ electrons and the H_2-type MO. This force from each O causes the H_2-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $2p$ electrons of each O decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of O_2 is $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^3 2p_2^3 \sigma_{1,2}^2$ where the subscript designates the O atom, 1 or 2, σ designates the H_2-type MO, and the orbital arrangement is



(13.667)

Oxygen is predicted to be paramagnetic in agreement with observations [42].

FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOMS OF THE OXYGEN MOLECULE

For each O atom, force balance for the outermost $2p$ electron of O_2 (electron 7) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 7 and the other $2p$-shell as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of O_2 (electron 7) due to the nucleus and the inner six electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-6)e^2}{4\pi\varepsilon_0 r_7^2}\mathbf{i}_r \tag{13.668}$$

for $r > r_6$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_7$. The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces are the same as those of the reactant oxygen atoms with r_7 replacing r_8. The diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contributions is given by Eq. (10.156):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}+\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{3\hbar^2}{12m_e r_7^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{13.669}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_7^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.670}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_7$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_7^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{13.671}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.688)) and diamagnetic (Eqs. (13.669) and (13.671)), and

paramagnetic (Eq. (13.670)) forces as follows:

$$\frac{m_e v_7^2}{r_7} = \begin{pmatrix} \frac{(Z-6)e^2}{4\pi\varepsilon_0 r_7^2} - \frac{3\hbar^2}{12 m_e r_7^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Z m_e r_7^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_7^4 m_e}10\sqrt{s(s+1)} \end{pmatrix} \tag{13.672}$$

Substitution of $v_7 = \frac{\hbar}{m_e r_7}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (13.672) gives:

$$\frac{\hbar^2}{m_e r_7^3} = \frac{(Z-6)e^2}{4\pi\varepsilon_0 r_7^2} - \frac{3\hbar^2}{12 m_e r_7^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Z m_e r_7^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_7^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.673}$$

The quadratic equation corresponding to Eq. (13.673) is

$$r_7^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-6)e^2}{4\pi\varepsilon_0} - \left(\frac{3}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_7 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-6)e^2}{4\pi\varepsilon_0} - \left(\frac{3}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.674}$$

The solution of Eq. (13.674) using the quadratic formula is:

$$r_7 = \frac{\frac{a_0}{\left((Z-6)-\left(\frac{3}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1}{\left((Z-6)-\left(\frac{3}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-7}{Z-6}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-6)-\left(\frac{3}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2} \tag{13.675}$$

r_3 *in units of* a_0

The positive root of Eq. (13.675) must be taken in order that $r_7 > 0$. Substitution of $\frac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (13.675) gives

$$r_7 = 0.91088 a_0 \tag{13.676}$$

ENERGIES OF THE $2p$ SHELL OF THE OXYGEN ATOMS OF THE

OXYGEN MOLECULE

The central forces on the $2p$ shell of each O are increased with the formation of the σ MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two O atoms at the new radius are calculated and added to the energy of the σ MO to give the total energy of O_2. Then, the bond energy is determined from the total O_2 energy.

The radius r_8 of each oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \tag{13.677}$$

Using the initial radius r_8 of each O atom and the final radius r_7 of the $O2p$ shell of O_2 (Eq. (13.676)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(O_2,2p)$ of the Coulombic energy change of the $O2p$ electrons of both atoms is determined using Eq. (10.102):

$$\begin{aligned} E_T(O_2,2p) &= -2\sum_{n=4}^{6}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_7}-\frac{1}{r_8}\right) \\ &= -2(13.60580\ eV)(0.09784)(2+3+4) \\ &= -23.96074\ eV \end{aligned} \tag{13.678}$$

FORCE BALANCE OF THE σ MO OF THE OXYGEN MOLECULE

The force balance equation for the σ-MO of the oxygen molecule given by Eq. (11.200) and Eqs. (13.633-13.634) with $n_e = 2$ and $|L| = \sqrt{\frac{3}{4}}\hbar$ is

$$\frac{\hbar^2}{m_e a^2 b^2}D = \frac{e^2}{8\pi\varepsilon_0 ab^2}D + \frac{\hbar^2}{2m_e a^2 b^2}D - \left(\frac{3}{2}+\frac{\sqrt{\frac{3}{4}}}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2}D \tag{13.679}$$

$$\frac{\hbar^2}{m_e a^2 b^2}D = \frac{e^2}{8\pi\varepsilon_0 ab^2}D - \left(\frac{1}{2}+\frac{\sqrt{\frac{3}{4}}}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2}D \tag{13.680}$$

$$\left(\frac{5}{2}+\frac{\sqrt{\frac{3}{4}}}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2}D = \frac{e^2}{8\pi\varepsilon_0 ab^2}D \tag{13.681}$$

$$a=\left(\frac{5}{2}+\frac{\sqrt{\frac{3}{4}}}{Z}\right)a_0 \tag{13.682}$$

Substitution of $Z=8$ into Eq. (13.682) gives

$$a=2.60825a_0=1.38023\,X\,10^{-10}\ m \tag{13.683}$$

Substitution of Eq. (13.683) into Eq. (11.79) is

$$c'=1.14198a_0=6.04312\,X\,10^{-11}\ m \tag{13.684}$$

The internuclear distance given by multiplying Eq. (13.684) by two is

$$2c'=2.28397a_0=1.20862\,X\,10^{-10}\ m \tag{13.685}$$

The experimental bond distance is [28]

$$2c'=1.20752\,X\,10^{-10}\ m \tag{13.686}$$

Substitution of Eqs. (13.683-13.684) into Eq. (11.80) is

$$b=c=2.34496a_0=1.24090\,X\,10^{-10}\ m \tag{13.687}$$

Substitution of Eqs. (13.683-13.684) into Eq. (11.67) is

$$e=0.43783 \tag{13.688}$$

Using the electron configuration of O_2 (Eq. (13.667)), the radii of the $O1s=0.12739a_0$ (Eq. (10.51)), $O2s=0.59020a_0$ (Eq. (10.62)), and $O2p=0.91088a_0$ (Eq. (13.676)) shells and the parameters of the σ MO of O_2 given by Eqs. (13.3-13.4), (13.683-13.685), and (13.687-13.688), the dimensional diagram and charge-density of the O_2 MO are shown in Figures 21 and 22, respectively.

SUM OF THE ENERGIES OF THE σ MO AND THE AOs OF THE OXYGEN MOLECULE

The energies of the O_2 σ MO are given by the substitution of the semiprincipal axes (Eqs. (13.683-13.684) and (13.687)) into the energy equations (Eqs. (11.207-11.212)) of H_2:

$$V_e=\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-22.37716\ eV \tag{13.689}$$

$$V_p=\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=11.91418\ eV \tag{13.690}$$

$$T=\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=4.28968\ eV \tag{13.691}$$

$$V_m=\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-2.14484\ eV \tag{13.692}$$

$$E_T=V_e+T+V_m+V_p \tag{13.693}$$

Substitution of Eqs. (11.79) and (13.689-13.692) into Eq. (13.693) gives

$$E_T(O_2,\sigma)=\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right)=-8.31814\ eV \tag{13.694}$$

where $E_T(O_2,\sigma)$ is the total energy of the σ MO of O_2. The sum, $E_T(O_2)$, of $E_T(O_2,2p)$, the $2p$ AO contribution given by Eq. (13.678), and $E_T(O_2,\sigma)$, the σ MO contribution given by Eq. (13.694) is:

$$\begin{aligned}E_T(O_2)&=E_T(O_2,2p)+E_T(O_2,\sigma)\\&=-23.96074\ eV-8.31814\ eV\\&=-32.27888\ eV\end{aligned} \tag{13.695}$$

VIBRATION OF O_2

The vibrational energy levels of O_2 may be solved by determining the Morse potential curve from the energy relationships for the transition from two O atoms whose parameters are given by Eqs. (10.154-10.163) to the two O atoms whose parameter r_7 is given by Eq. (13.676) and the σ MO whose parameters are given by Eqs. (13.683-13.685) and (13.687-13.688). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF THE OXYGEN MOLECULE

The equations of the radiation reaction force of oxygen are the same as those of H_2 with the substitution of the oxygen parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 9.81432\,X\,10^{16}\ rad/s \tag{13.696}$$

where a is given by Eq. (13.683). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 9.81432\,X\,10^{16}\ rad/s = 6.45996\ eV \tag{13.697}$$

In Eq. (11.181), substitution of $E_T(O_2)$ for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.697) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -32.27888\ eV\sqrt{\frac{2e(6.45996\ eV)}{m_e c^2}} = -0.16231\ eV \tag{13.698}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the O_2 MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.698) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental O_2 ω_e of 1580.19 cm^{-1} $(0.19592\ eV)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(O_2)$ is

$$\overline{E}_{osc}(O_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.699}$$

$$\overline{E}_{osc}(O_2) = -0.16231\ eV + \frac{1}{2}(0.19592\ eV) = -0.06435\ eV \tag{13.700}$$

TOTAL AND BOND ENERGIES OF THE OXYGEN MOLECULE

$E_{T+osc}(O_2)$, the total energy of O_2 including the Doppler term, is given by the sum of $E_T(O_2)$ (Eq. (13.695)) and $\overline{E}_{osc}(O_2)$ given by Eq. (13.700):

$$E_{T+osc}(O_2) = V_e + T + V_m + V_p + E_T(O_2, 2p) + \bar{E}_{osc}(O_2)$$
$$= E_T(O_2, \sigma) + E_T(O_2, 2p) + \bar{E}_{osc}(O_2) \quad (13.701)$$
$$= E_T(O_2) + \bar{E}_{osc}(O_2)$$

$$E_{T+osc}(O_2) = \left\{ \begin{array}{l} \left(\frac{-e^2}{8\pi\varepsilon_0 \sqrt{\frac{aa_0}{2}}} \left(\left(2 - \frac{1}{2}\frac{a_0}{a}\right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) - 2\sum_{n=4}^{6} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_7} - \frac{1}{r_8} \right) \right) \\ \left(1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}} \right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{array} \right\} \quad (13.702)$$
$$= -32.27888\ eV - 0.16231\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

From Eqs. (13.699-13.702), the total energy of the O_2 MO is

$$E_{T+osc}(O_2) = -32.27888\ eV + \bar{E}_{osc}(O_2)$$
$$= -32.27888\ eV - 0.16231\ eV + \frac{1}{2}(0.19592\ eV) \quad (13.703)$$
$$= -32.34323\ eV$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The O_2 bond dissociation energy, $E_D(O_2)$, is given by the difference in the total energies of the two O atoms and $E_{T+osc}(O_2)$:

$$E_D(O_2) = 2E(O) - E_{T+osc}(O_2) \quad (13.704)$$

where the energy of an oxygen atom is [6]

$$E(O) = -13.61806\ eV \quad (13.705)$$

Thus, the O_2 bond dissociation energy, $E_D(O_2)$, given by Eqs. (13.703-13.705) is

$$E_D(O_2) = -2(13.61806\ eV) - E_{T+osc}(O_2)$$
$$= -27.23612\ eV - (-32.34323\ eV) \quad (13.706)$$
$$= 5.10711\ eV$$

The experimental O_2 bond dissociation energy from Ref. [46] and Ref. [47] is

$$E_D(O_2) = 5.11665\ eV \quad (13.707)$$

$$E_D(O_2) = 5.116696\ eV \quad (13.708)$$

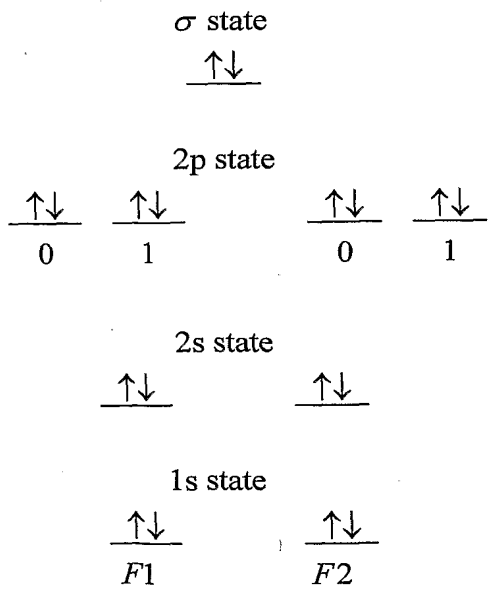
The results of the determination of bond parameters of O_2 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

FLUORINE MOLECULE

The fluorine molecule can be formed by the reaction of two fluorine atoms:

$$F + F \rightarrow F_2 \tag{13.709}$$

The bond in the fluorine molecule comprises a H_2-type molecular orbital (MO) with two paired electrons. The force balance equation and radius r_9 of the $2p$ shell of F is derived in the Nine-Electron Atoms section. With the formation of the H_2-type MO by the contribution of a $2p$ electron from each F atom, a diamagnetic force arises between the remaining $2p$ electrons and the H_2-type MO. This force from each F causes the H_2-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $2p$ electrons of each F decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of F_2 is $1s_1^2 1s_2^2 2s_1^2 2s_2^2 2p_1^4 2p_2^4 \sigma_{1,2}^2$ where the subscript designates the F atom, 1 or 2, σ designates the H_2-type MO, and the orbital arrangement is



(13.710)

Fluorine is predicted to be diamagnetic in agreement with observations [42].

FORCE BALANCE OF THE $2p$ SHELL OF THE FLUORINE ATOMS OF THE FLUORINE MOLECULE

For each F atom, force balance for the outermost $2p$ electron of F_2 (electron 8) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 8 and the other $2p$-shell as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Nine-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of F_2 (electron 8) due to the nucleus and the inner seven electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-7)e^2}{4\pi\varepsilon_0 r_8^2}\mathbf{i}_r \tag{13.711}$$

for $r > r_7$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_8$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contributions is the same as that of the reactant fluorine atoms given by Eq. (10.176) with r_8 replacing r_9:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_8^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{13.712}$$

Thus, $\mathbf{F}_{diamagnetic}$ due to the two filled $2p$ orbitals per F atom is twice that of N_2 given by Eq. (13.622) having one filled $2p$ orbital per N atom. $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum is also the same as that of the reactant fluorine atoms given by Eq. (10.177) and that of N_2 given by Eq. (13.623) where the outer radius of the $2p$ shell of the F atoms of F_2 is r_8.

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_8^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.713}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_8$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_8^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{13.714}$$

In addition, the contribution of a $2p$ electron from each F atom in the formation of the σ MO gives rise to a paramagnetic force on the remaining paired $2p$ electrons. The force $\mathbf{F}_{mag\ 3}$ is given by Eq. (13.625) wherein the radius is r_8:

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_8^3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.715}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.711)) and diamagnetic (Eqs. (13.712) and (13.714)), and paramagnetic (Eqs. (13.713) and (13.715)) forces as follows:

$$\frac{m_e v_8^2}{r_8} = \left(\begin{array}{l}\frac{(Z-7)e^2}{4\pi\varepsilon_0 r_8^2} - \frac{2\hbar^2}{12m_e r_8^2 r_3}\sqrt{s(s+1)} + \frac{3\hbar^2}{Zm_e r_8^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_8^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_8^3}\sqrt{s(s+1)}\end{array}\right) \tag{13.716}$$

Substitution of $v_8 = \frac{\hbar}{m_e r_8}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (13.716) gives:

$$\frac{\hbar^2}{m_e r_8^3} - \frac{\hbar^2}{4m_e r_8^3}\sqrt{\frac{3}{4}} = \frac{(Z-7)e^2}{4\pi\varepsilon_0 r_8^2} - \frac{2\hbar^2}{12m_e r_8^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Zm_e r_8^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_8^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.717}$$

The quadratic equation corresponding to Eq. (13.717) is

$$r_8^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)}r_8 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-8}{Z-7}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-7)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.718}$$

The solution of Eq. (13.718) using the quadratic formula is:

$$r_8 = \frac{\dfrac{a_0\left(1-\dfrac{\sqrt{3}}{8}\right)}{\left((Z-7)-\left(\dfrac{2}{12}-\dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\dfrac{1-\dfrac{\sqrt{3}}{8}}{\left((Z-7)-\left(\dfrac{2}{12}-\dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-8}{Z-7}\right]\left(1-\dfrac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-7)-\left(\dfrac{2}{12}-\dfrac{3}{Z}\right)\dfrac{\sqrt{3}}{2r_3}\right)}}}{2} \qquad (13.719)$$

r_3 *in units of* a_0

The positive root of Eq. (13.719) must be taken in order that $r_8 > 0$. Substitution of $\frac{r_3}{a_0} = 0.51382$ (Eq. (10.62) with $Z = 9$) into Eq. (13.719) gives

$$r_8 = 0.73318a_0 \qquad (13.720)$$

ENERGIES OF THE $2p$ SHELL OF THE FLUORINE ATOMS OF THE FLUORINE MOLECULE

The central forces on the $2p$ shell of each F are increased with the formation of the σ MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the two F atoms at the new radius are calculated and added to the energy of the σ MO to give the total energy of F_2. Then, the bond energy is determined from the total F_2 energy.

The radius r_9 of each fluorine atom before bonding is given by Eq. (10.182):

$$r_9 = 0.78069a_0 \qquad (13.721)$$

Using the initial radius r_9 of each F atom and the final radius r_8 of the $F2p$ shell of F_2 (Eq. (13.720)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(F_2, 2p)$ of the Coulombic energy change of the $F2p$ electrons of both atoms is determined using Eq. (10.102):

$$\begin{aligned} E_T(F_2, 2p) &= -2\sum_{n=4}^{7}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_8}-\frac{1}{r_9}\right) \\ &= -2(13.60580\ eV)(0.08301)(2+3+4+5) \\ &= -31.62353\ eV \end{aligned} \qquad (13.722)$$

FORCE BALANCE OF THE σ MO OF THE FLUORINE MOLECULE

The relativistic diamagnetic force $\mathbf{F}_{diamagneticMO2}$ of F_2 is one half that of N_2 due to the two versus one filled $2p$ orbitals per atom at the focus. The force balance equation for the σ-MO of the fluorine molecule is given by Eq. (11.200) and Eqs. (13.633-13.634) with the correction of 1/2 due the two $2p$ orbitals per F after Eqs. (10.2-10.11), $n_e = 2$, and $|L| = \hbar$:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(\frac{5}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.723}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D - \left(\frac{3}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.724}$$

$$\left(\frac{7}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D \tag{13.725}$$

$$a = \left(\frac{7}{2} + \frac{1}{2Z}\right) a_0 \tag{13.726}$$

Substitution of $Z = 9$ into Eq. (13.726) gives

$$a = 3.55556 a_0 = 1.88152\, X\, 10^{-10}\ m \tag{13.727}$$

Substitution of Eq. (13.727) into Eq. (11.79) is

$$c' = 1.33333 a_0 = 7.05569\, X\, 10^{-11}\ m \tag{13.728}$$

The internuclear distance given by multiplying Eq. (13.728) by two is

$$2c' = 2.66667 a_0 = 1.41114\, X\, 10^{-10}\ m \tag{13.729}$$

The experimental bond distance is [28]

$$2c' = 1.41193\, X\, 10^{-10}\ m \tag{13.730}$$

Substitution of Eqs. (13.727-13.728) into Eq. (11.80) is

$$b = c = 3.29609 a_0 = 1.74421\, X\, 10^{-10}\ m \tag{13.731}$$

Substitution of Eqs. (13.727-13.728) into Eq. (11.67) is

$$e = 0.37500 \tag{13.732}$$

Using the electron configuration of F_2 (Eq. (13.710)), the radii of the $F1s = 0.11297 a_0$ (Eq. (10.51)), $F2s = 0.51382 a_0$ (Eq. (10.62)), and $F2p = 0.73318 a_0$ (Eq. (13.720)) shells and the parameters of the σ MO of F_2 given by Eqs. (13.3-13.4), (13.727-13.728), and (13.731-13.732), the dimensional diagram and charge-density of the F_2 MO are shown in Figures 23 and 24, respectively.

SUM OF THE ENERGIES OF THE σ MO AND THE AOs OF THE FLUORINE MOLECULE

The energies of the F_2 σ MO are given by the substitution of the semiprincipal axes (Eqs. (13.683-13.684) and (13.687)) into the energy equations (Eqs. (11.207-11.212)) of H_2:

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.09139\ eV \tag{13.733}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 10.20435\ eV \tag{13.734}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 2.26285\ eV \tag{13.735}$$

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -1.13143\ eV \tag{13.736}$$

$$E_T = V_e + T + V_m + V_p \tag{13.737}$$

Substitution of Eqs. (11.79) and (13.733-13.736) into Eq. (13.737) gives

$$E_T(F_2,\sigma) = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right) = -4.75562\ eV \tag{13.738}$$

where $E_T(F_2,\sigma)$ is the total energy of the σ MO of F_2. The sum, $E_T(F_2)$, of $E_T(F_2,2p)$, the $2p$ AO contribution given by Eq. (13.722), and $E_T(F_2,\sigma)$, the σ MO contribution given by Eq. (13.738) is:

$$\begin{aligned} E_T(F_2) &= E_T(F_2,2p) + E_T(F_2,\sigma) \\ &= -31.62353\ eV - 4.75562\ eV \\ &= -36.37915\ eV \end{aligned} \tag{13.739}$$

VIBRATION OF F_2

The vibrational energy levels of F_2 may be solved by determining the Morse potential curve from the energy relationships for the transition from two F atoms whose parameters are given by Eqs. (10.174-10.183) to the two F atoms whose parameter r_8 is given by Eq.

(13.720) and the σ MO whose parameters are given by Eqs. (13.727-13.729) and (13.731-13.732). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF THE FLUORINE MOLECULE

The equations of the radiation reaction force of fluorine are the same as those of H_2 with the substitution of the fluorine parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 6.16629\,X\,10^{15}\ rad/s \tag{13.740}$$

where a is given by Eq. (13.727). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 6.16629\,X\,10^{15}\ rad/s = 4.05876\ eV \tag{13.741}$$

In Eq. (11.181), substitution of $E_T(F_2)$ for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.741) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -36.37915\ eV\sqrt{\frac{2e(4.05876\ eV)}{m_e c^2}} = -0.14499\ eV \tag{13.742}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the F_2 MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.742) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental F_2 ω_e of 916.64 cm^{-1} (0.11365 eV) [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(F_2)$ is

$$\overline{E}_{osc}(F_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.743}$$

$$\overline{E}_{osc}(F_2) = -0.14499\ eV + \frac{1}{2}(0.11365\ eV) = -0.08817\ eV \tag{13.744}$$

TOTAL AND BOND ENERGIES OF THE FLUORINE MOLECULE

$E_{T+osc}(F_2)$, the total energy of F_2 including the Doppler term, is given by the sum of $E_T(F_2)$ (Eq. (13.739)) and $\overline{E}_{osc}(F_2)$ given by Eq. (13.744):

$$\begin{aligned} E_{T+osc}(F_2) &= V_e + T + V_m + V_p + E_T(F_2, 2p) + \overline{E}_{osc}(F_2) \\ &= E_T(F_2, \sigma) + E_T(F_2, 2p) + \overline{E}_{osc}(F_2) \\ &= E_T(F_2) + \overline{E}_{osc}(F_2) \end{aligned} \tag{13.745}$$

$$\begin{aligned} E_{T+osc}(F_2) &= \left\{ \begin{array}{l} \left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left(\left(2 - \frac{1}{2}\frac{a_0}{a}\right) \ln \frac{a + \sqrt{\frac{aa_0}{2}}}{a - \sqrt{\frac{aa_0}{2}}} - 1 \right) - 2\sum_{n=4}^{7} \frac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\frac{1}{r_8} - \frac{1}{r_9} \right) \right) \\ \left(1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}} \right) + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{array} \right. \\ &= -36.37915\ eV - 0.14499\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.746}$$

From Eqs. (13.743-13.746), the total energy of the F_2 MO is

$$\begin{aligned} E_{T+osc}(F_2) &= -36.37915\ eV + \overline{E}_{osc}(F_2) \\ &= -36.37915\ eV - 0.14499\ eV + \frac{1}{2}(0.11365\ eV) \\ &= -36.46732\ eV \end{aligned} \tag{13.747}$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The F_2 bond dissociation energy, $E_D(F_2)$, is given by the difference in the total energies of the two F atoms and $E_{T+osc}(F_2)$:

$$E_D(F_2) = 2E(F) - E_{T+osc}(F_2) \tag{13.748}$$

where the energy of a fluorine atom is [6]

$$E(F) = -17.42282\ eV \tag{13.749}$$

Thus, the F_2 bond dissociation energy, $E_D(F_2)$, given by Eqs. (13.747-13.749) is

$$\begin{aligned} E_D(F_2) &= -2(17.42282\ eV) - E_{T+osc}(F_2) \\ &= -34.84564\ eV - (-36.46732\ eV) \\ &= 1.62168\ eV \end{aligned} \tag{13.750}$$

The experimental F_2 bond dissociation energy is [48]

$$E_D(F_2) = 1.606\ eV \tag{13.751}$$

The results of the determination of bond parameters of F_2 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

CHLORINE MOLECULE

The chlorine molecule can be formed by the reaction of two chlorine atoms:

$$Cl + Cl \rightarrow Cl_2 \tag{13.752}$$

The chlorine molecule can be solved by using the hybridization approach used to solve the methane series $CH_{n=1,2,3,4}$. In the methane series, the $2s$ and $2p$ shells of carbon hybridize to form a single $2sp^3$ shell to achieve an energy minimum, and in a likewise manner, the $3s$ and $3p$ shells of chlorine hybridize to form a single $3sp^3$ shell which forms the bonding orbital of Cl_2.

FORCE BALANCE OF Cl_2

Cl_2 has two spin-paired electrons in a chemical bond between the chlorine atoms. The Cl_2 molecular orbital (MO) is determined by considering properties of the binding atoms and the boundary constraints. The prolate spheroidal H_2 MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules section satisfies the boundary constraints; thus, each Cl atom could contribute a $3p$ electron to form a σ MO (H_2-type ellipsoidal MO) as in the case of N_2, O_2, and F_2. However, such a bond is not possible with the outer Cl electrons in their ground state since the resulting $3p$ shells of chlorine atoms would overlap which is not energetically stable. Thus, when bonding, the chlorine $3s$ and $3p$ shells

hybridize to form a single $3sp^3$ shell to achieve an energy minimum.

The Cl electron configuration given in the Seventeen-Electron Atoms section is $1s^2 2s^2 2p^6 3s^2 3p^5$, and the orbital arrangement is

$$\begin{array}{c} \text{3p state} \\ \underline{\uparrow\downarrow} \quad \underline{\uparrow\downarrow} \quad \underline{\uparrow} \\ 1 \quad 0 \quad -1 \end{array} \tag{13.753}$$

corresponding to the ground state ${}^2P^0_{3/2}$. The radius r_{17} of the $3p$ shell given by Eq. (10.363) is

$$r_{17} = 1.05158 a_0 \tag{13.754}$$

The energy of the chlorine $3p$ shell is the negative of the ionization energy of the chlorine atom given by Eq. (10.364). Experimentally, the energy is [6]

$$E(3p\ shell) = -E(ionization;\ Cl) = -12.96764\ eV \tag{13.755}$$

The $Cl3s$ atomic orbital (AO) combines with the $Cl3p$ AOs to form a single $3sp^3$ hybridized orbital (HO) with the orbital arrangement

$$\begin{array}{c} \text{2sp}^3\text{ state} \\ \underline{\uparrow\downarrow} \quad \underline{\uparrow\downarrow} \quad \underline{\uparrow\downarrow} \quad \underline{\uparrow} \\ 0,0 \quad 1,-1 \quad 1,0 \quad 1,1 \end{array} \tag{13.756}$$

where the quantum numbers (ℓ, m_ℓ) are below each electron. The total energy of the state is given by the sum over the seven electrons. Using only the largest-force terms of the outer most and next inner shell, the calculated energies for the chlorine atom and the ions: Cl, Cl^+, Cl^{2+}, Cl^{3+}, Cl^{4+}, Cl^{5+} and Cl^{6+} are given in Eqs. (10.363-10.364), (10.353-10.354), (10.331-10.332), (10.309-10.310), (10.288-10.289), (10.255-10.256), and (10.235-10.236), respectively. The sum $E_T(Cl, 3sp^3)$ of the experimental energies of Cl and these ions is [6]

$$\begin{aligned} E_T(Cl, 3sp^3) &= \begin{pmatrix} 12.96764\ eV + 23.814\ eV + 39.61\ eV + 53.4652\ eV \\ +67.8\ eV + 97.03\ eV + 114.1958\ eV \end{pmatrix} \\ &= 408.88264\ eV \end{aligned} \tag{13.757}$$

The spin and orbital-angular-momentum interactions cancel such that the energy of the $E_T(Cl, 3sp^3)$ is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius r_{3sp^3} of the $Cl3sp^3$ shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{3sp^3} = \sum_{n=10}^{16} \frac{(Z-n)e^2}{8\pi\varepsilon_0 (e408.8826\ eV)} = \frac{28e^2}{8\pi\varepsilon_0 (e408.8826\ eV)} = 0.93172a_0 \quad (13.758)$$

where $Z = 17$. Using Eqs. (10.102) and (13.758), the Coulombic energy $E_{Coulomb}(Cl, 3sp^3)$ of the outer electron of the $Cl3sp^3$ shell is

$$E_{Coulomb}(Cl, 3sp^3) = \frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.93172a_0} = -14.60295\ eV \quad (13.759)$$

The calculated energy of the $C2sp^3$ shell of $14.63489\ eV$ given by Eq. (13.428), and nitrogen's calculated energy of $14.61664\ eV$ given by Eq. (10.143) is a close match with $E_{Coulomb}(Cl, 3sp^3)$.

The unpaired $Cl3sp^3$ electron from each of two chlorine atoms combine to form a molecular orbital. The nuclei of the Cl atoms are along the internuclear axis and serve as the foci. Due to symmetry, the other Cl electrons are equivalent to point charges at the origin. (See Eqs. (19-38) of Appendix IV.) Thus, the energies in the Cl MO involve only the two $Cl3sp^3$ electrons. The forces are determined by these energies.

As in the case of H_2, the MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $Cl3sp^3$ HO for distances shorter than the radius of the $Cl3sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the nuclei and is continuous with the $Cl3sp^3$ shell at each Cl atom. The energy of the H_2-type ellipsoidal MO is matched to that of the $Cl3sp^3$ shell. As in the case with OH, NH, and CH (where the latter also demonstrates sp^3 hybridization) the linear combination of the H_2-type ellipsoidal MO with each $Cl3sp^3$ HO must involve a 25% contribution from the H_2-type ellipsoidal MO to the $Cl3sp^3$ HO in order to match potential, kinetic, and orbital energy relationships. Thus, the Cl_2 MO must comprise two $Cl3sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the two $Cl3sp^3$ HOs:

$$2\ Cl3sp^3 + 0.75\ H_2\ MO \rightarrow Cl_2\ MO \quad (13.760)$$

The force balance of the Cl_2 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.760) and the energy matching condition between the H_2-type-ellipsoidal-MO and $Cl3sp^3$-HO components of the MO.

As in the case with OH (Eq. (13.57)), NH (Eq. (13.247)), and CH (Eq. 13.429)), the H_2-type ellipsoidal MO comprises 75% of the Cl_2 MO; so, the electron charge density in Eq. (11.65) is given by $-0.75e$. Since the chlorine atoms of Cl_2 are hybridized and the k parameter is different from unity in order to meet the boundary constraints, both k and k' must comprise the corresponding hybridization factors. (In contrast, the chlorine atom of a $C-Cl$ bond of an alkyl chloride is not hybridized, and only k' must comprise the corresponding hybridization factor.) The force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci is given by Eq. (13.59), except that k' is divided by two since the H_2-type-ellipsoidal-MO is physically divided between two $Cl3sp^3$ HOs. In addition, the energy matching at both $Cl3sp^3$ HOs further requires that k' be corrected the hybridization factor given by Eq. (13.762). Thus, k' of the H_2-type-ellipsoidal-MO component of the Cl_2 MO is

$$k' = C_{Cl3sp^3HO}\frac{(0.75)}{2}\frac{2e^2}{4\pi\varepsilon_0} = 0.93172\frac{(0.75)}{2}\frac{2e^2}{4\pi\varepsilon_0} \tag{13.761}$$

The distance from the origin to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $Cl-Cl$-bond $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the Cl_2 MO. Since the Cl_2 MO comprises a H_2-type-ellipsoidal MO that transitions to the $Cl3sp^3$ HOs at each end of the molecule, the energy $E\left(Cl,3sp^3\right)$ in Eq. (13.759) adds to that of the H_2-type ellipsoidal MO to give the total energy of the Cl_2 MO. From the energy equation and the relationship between the axes, the dimensions of the Cl_2 MO are solved.

The energy components of V_e, V_p, T, and V_m are those of H_2 (Eqs. (11.207-11.211)) except that they are corrected for electron hybridization. Hybridization gives rise to the $Cl3sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(Cl,3sp^3\right)$ given by Eq. (13.759). To meet the

equipotential condition of the union of the H_2-type-ellipsoidal-MO with each $Cl3sp^3$ HO, the electron energies are normalized by the ratio of $14.60295\,eV$, the magnitude of $E_{Coulomb}\left(Cl,3sp^3\right)$ given by Eq. (13.759), and $13.605804\,eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). This normalizes the energies to match that of the Coulombic energy alone to meet the energy matching condition of the Cl_2 MO under the influence of the two $Cl3sp^3$ HOs bridged by the H_2-type-ellipsoidal MO. The hybridization energy factor C_{Cl3sp^3HO} is

$$C_{Cl3sp^3HO}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{3sp^3}}}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.93172 a_0}}=\frac{13.605804\,eV}{14.60295\,eV}=0.93172 \tag{13.762}$$

The total energy $E_T\left(Cl_2\right)$ of the Cl_2 MO is given by the sum of the energies of the orbitals, the H_2-type ellipsoidal MO and the two $Cl3sp^3$ HOs, that form the hybridized Cl_2 MO. $E_T\left(Cl_2\right)$ follows from by Eq. (13.74) for OH, but the energy of the $Cl3sp^3$ HO given by Eq. (13.759) is substituted for the energy of O and the H_2-type-ellipsoidal-MO energies are those of H_2 (Eqs. (11.207-11.212)) multiplied by the electron hybridization factor rather than by the factor of 0.75:

$$\begin{aligned}E_T\left(Cl_2\right)&=E_T+E_{Coulomb}\left(Cl,3sp^3\right)\\&=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.93172)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.60295\,eV\end{aligned} \tag{13.763}$$

To match the boundary condition that the total energy of the entire the H_2-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_T\left(Cl_2\right)$ given by Eq. (13.763) is set equal to Eq. (13.75):

$$E_T\left(Cl_2\right)=-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.93172)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.60295\,eV=-31.63537\,eV \tag{13.764}$$

From the energy relationship given by Eq. (13.764) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the Cl_2 MO can be solved.

Substitution of Eqs. (13.60) and (13.761) into Eq. (13.764) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{4aa_0}{3(0.93172)}}}\left[(0.93172)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{4aa_0}{3(0.93172)}}}{a-\sqrt{\frac{4aa_0}{3(0.93172)}}}-1\right]=e17.03242$$

(13.765)

The most convenient way to solve Eq. (13.765) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=2.46500a_0=1.30442\,X\,10^{-10}\ m \tag{13.766}$$

Substitution of Eq. (13.766) into Eq. (13.60) gives

$$c'=1.87817a_0=9.93887\,X\,10^{-11}\ m \tag{13.767}$$

The internuclear distance given by multiplying Eq. (13.767) by two is

$$2c'=3.75635a_0=1.98777\,X\,10^{-10}\ m \tag{13.768}$$

The experimental bond distance is [28]

$$2c'=1.988\,X\,10^{-10}\ m \tag{13.769}$$

Substitution of Eqs. (13.766-13.767) into Eq. (13.62) gives

$$b=c=1.59646a_0=8.44810\,X\,10^{-11}\ m \tag{13.770}$$

Substitution of Eqs. (13.766-13.767) into Eq. (13.63) gives

$$e=0.76194 \tag{13.771}$$

The Cl nuclei comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $Cl3sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n=r_{3sp^3}=0.93172a_0$ is the radius of the $Cl3sp^3$ shell. Substitution of Eqs. (13.766-13.767) into Eq. (13.261) gives

$$\theta'=81.72° \tag{13.772}$$

Then, the angle θ_{Cl3sp^3HO} the radial vector of the $Cl3sp^3$ HO makes with the internuclear axis is

$$\theta_{Cl3sp^3HO}=180°-81.72°=98.28° \tag{13.773}$$

as shown in Figure 25. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t=\theta_{H_2MO}$

between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $Cl3sp^3$ radial vector obeys the following relationship:

$$r_{3sp^3}\sin\theta_{Cl3sp^3HO} = 0.93172a_0\sin\theta_{Cl3sp^3HO} = b\sin\theta_{H_2MO} \tag{13.774}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.93172a_0\sin\theta_{Cl3sp^3HO}}{b} = \sin^{-1}\frac{0.93172a_0\sin 98.28°}{b} \tag{13.775}$$

with the use of Eq. (13.773). Substitution of Eq. (13.770) into Eq. (13.775) gives

$$\theta_{H_2MO} = 35.28° \tag{13.776}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{13.777}$$

Substitution of Eqs. (13.766) and (13.776) into Eq. (13.777) gives

$$d_{H_2MO} = 2.01235a_0 = 1.06489\,X\,10^{-10}\ m \tag{13.778}$$

The distance d_{Cl3sp^3HO} along the internuclear axis from the origin of each Cl atom to the point of intersection of the orbitals is given by

$$d_{Cl3sp^3HO} = d_{H_2MO} - c' \tag{13.779}$$

Substitution of Eqs. (13.768) and (13.778) into Eq. (13.779) gives

$$d_{Cl3sp^3HO} = 0.13417a_0 = 7.10022\,X\,10^{-12}\ m \tag{13.780}$$

As shown in Eq. (13.760), a factor of 0.25 of the charge-density of the H_2-type ellipsoidal MO is distributed on each $Cl3sp^3$ HO. Using the orbital composition of Cl_2 (Eq. (13.760)), the radii of the $Cl1s = 0.05932a_0$ (Eq. (10.51)), $Cl2s = 0.25344a_0$ (Eq. (10.62)), $Cl2p = 0.31190a_0$ (Eq. (10.212)), and $Cl3sp^3 = 0.93172a_0$ (Eq. (13.758)) shells, and the parameters of the Cl_2 MO given by Eqs. (13.3-13.4), (13.766-13.768), and (13.770-13.771), the dimensional diagram and charge-density of the Cl_2 MO comprising the linear combination of the H_2-type ellipsoidal MO and two $Cl3sp^3$ HOs according to Eq. (13.760) are shown in Figures 25 and 26, respectively.

ENERGIES OF Cl_2

The energies of Cl_2 are given by the substitution of the semiprincipal axes (Eqs. (13.766-13.767) and (13.770)) into the energy equations, (Eq. (13.763) and Eqs. (11.207-11.211) of H_2) that are corrected for electron hybridization using Eq. (13.762):

$$V_e = (0.93172)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -27.02007\ eV \tag{13.781}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 7.24416\ eV \tag{13.782}$$

$$T = (0.93172)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 5.48074\ eV \tag{13.783}$$

$$V_m = (0.93172)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -2.74037\ eV \tag{13.784}$$

$$E_T\left({}^{35}Cl_2\right) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.93172)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.60295\ eV = -31.63849\ eV \tag{13.785}$$

where $E_T(Cl_2)$ is given by Eq. (13.763) which is reiteratively matched to Eq. (13.75) within five-significant-figure round-off error.

VIBRATION AND ROTATION OF Cl_2

In Cl_2, the division of the H_2-type ellipsoidal MO between the two $Cl3sp^3$ HOs and the hybridization must be considered in determining the vibrational parameters. One approach is to use Eq. (13.761) for the force constant and r_{3sp^3} given by Eq. (13.758) for the distance parameter of the central force in Eq. (11.213) since the H_2-type ellipsoidal MO is energy matched to the $Cl3sp^3$ HOs. With the substitution of the Cl_2 parameters in Eqs. (11.213-11.217), the angular frequency of the oscillation is

$$\omega = \sqrt{\frac{0.93172\frac{(0.75)}{2}\frac{e^2}{8\pi\varepsilon_0\left(r_{3sp^3}\right)^3} - \frac{e^2}{8\pi\varepsilon_0\left(r_{3sp^3}+c'\right)^3}}{\mu}}$$
$$= \sqrt{\frac{0.93172\frac{(0.75)}{2}\frac{e^2}{8\pi\varepsilon_0(0.93172)^3} - \frac{e^2}{8\pi\varepsilon_0(0.93172a_0+1.87817a_0)^3}}{\frac{35}{2}m_p}} \quad (13.786)$$
$$= 1.01438\,X\,10^{14}\ rad/s$$

where c' is given by Eq. (13.767), and the reduced mass of $^{35}Cl_2$ is given by:

$$\mu_{^{35}Cl_2} = \frac{m_1 m_2}{m_1+m_2} = \frac{(35)(35)}{35+35}m_p \quad (13.787)$$

where m_p is the proton mass. Thus, during bond formation, the perturbation of the orbit determined by an inverse-squared force results in simple harmonic oscillatory motion of the orbit, and the corresponding frequency, $\omega(0)$, for $^{35}Cl_2$ given by Eqs. (11.136), (11.148), and (13.786) is

$$\omega(0) = \sqrt{\frac{k(0)}{\mu}} = \sqrt{\frac{301.19\ Nm^{-1}}{\mu}} = 1.01438\,X\,10^{14}\ radians/s \quad (13.788)$$

where the reduced nuclear mass of $^{35}Cl_2$ is given by Eq.(13.787) and the spring constant, $k(0)$, given by Eqs. (11.136) and (13.786) is

$$k(0) = 301.19\ Nm^{-1} \quad (13.789)$$

The $^{35}Cl_2$ transition-state vibrational energy, $E_{vib}(0)$ or ω_e, given by Planck's equation (Eq. (11.127)) is:

$$E_{vib}(0) = \omega_e = \hbar\omega = \hbar 1.01438\,X\,10^{14}\ rad/s = 0.06677\ eV = 538.52\ cm^{-1} \quad (13.790)$$

ω_e, from the experimental curve fit of the vibrational energies of $^{35}Cl_2$ is [28]

$$\omega_e = 559.7\ cm^{-1} \quad (13.791)$$

Using Eqs. (13.112-13.118) with $E_{vib}(0)$ given by Eq. (13.790) and D_0 given by Eq. (13.807), the $^{35}Cl_2$ $\upsilon = 1 \rightarrow \upsilon = 0$ vibrational energy, $E_{vib}(1)$ is

$$E_{vib}(1) = 0.0659\ eV \qquad \left(531.70\ cm^{-1}\right) \quad (13.792)$$

The experimental vibrational energy of $^{35}Cl_2$ using ω_e and $\omega_e x_e$ [28] according to K&P [15] is

$$E_{vib}(1) = 0.0664\ eV \qquad \left(535.55\ cm^{-1}\right) \tag{13.793}$$

Using Eq. (13.113) with $E_{vib}(1)$ given by Eq. (13.792) and D_0 given by Eq. (13.807), the anharmonic perturbation term, $\omega_0 x_0$, of $^{35}Cl_2$ is

$$\omega_0 x_0 = 3.41\ cm^{-1} \tag{13.794}$$

The experimental anharmonic perturbation term, $\omega_0 x_0$, of $^{35}Cl_2$ [28] is

$$\omega_0 x_0 = 2.68\ cm^{-1} \tag{13.795}$$

The vibrational energies of successive states are given by Eqs. (13.790), (13.112), and (13.794).

Using Eqs. (13.133-13.134) and the internuclear distance, $r = 2c'$, and reduced mass of $^{35}Cl_2$ given by Eqs. (13.768) and (13.787), respectively, the corresponding B_e is

$$B_e = 0.2420\ cm^{-1} \tag{13.796}$$

The experimental B_e rotational parameter of $^{35}Cl_2$ is [28]

$$B_e = 0.2440\ cm^{-1} \tag{13.797}$$

THE DOPPLER ENERGY TERMS OF Cl_2

The equations of the radiation reaction force of the symmetrical Cl_2 MO are the given by Eqs. (11.231-11.233) with the substitution of the Cl_2 parameters and the substitution of the force factor of Eq. (13.761). The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.93172\frac{(0.75)}{2}\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 6.31418\,X\,10^{15}\ rad/s \tag{13.798}$$

where a is given by Eq. (13.766). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 1.6.31418\,X\,10^{15}\ rad/s = 4.15610\ eV \tag{13.799}$$

In Eq. (11.181), substitution of the total energy of Cl_2, $E_T(Cl_2)$, (Eq. (13.764)) for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.799) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(4.15610\ eV)}{m_e c^2}} = -0.12759\ eV \tag{13.800}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of Cl_2 due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.800) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of Cl_2. Using the experimental $^{35}Cl_2$ ω_e of 559.7 cm^{-1} $(0.06939\ eV)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}\left(^{35}Cl_2\right)$ is

$$\overline{E}_{osc}\left(^{35}Cl_2\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.801}$$

$$\overline{E}_{osc}\left(^{35}Cl_2\right) = -0.12759\ eV + \frac{1}{2}(0.06939\ eV) = -0.09289\ eV \tag{13.802}$$

TOTAL AND BOND ENERGIES OF Cl_2

$E_{T+osc}\left(^{35}Cl_2\right)$, the total energy of the $^{35}Cl_2$ radical including the Doppler term, is given by the sum of $E_T(Cl_2)$ (Eq. (13.764)) and $\overline{E}_{osc}\left(^{35}Cl_2\right)$ given by Eq. (13.802):

$$\begin{aligned} E_{T+osc}\left(^{35}Cl_2\right) &= V_e + T + V_m + V_p + E_{Coulomb}\left(Cl, 3sp^3\right) + \overline{E}_{osc}\left(^{35}Cl_2\right) \\ &= E_T(Cl_2) + \overline{E}_{osc}\left(^{35}Cl_2\right) \end{aligned} \tag{13.803}$$

$$\begin{aligned} E_{T+osc}\left(^{35}Cl_2\right) &= \left\{\left(\frac{-e^2}{8\pi\varepsilon_0 c'}\left[(0.93172)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-14.60295\ eV\right)\right. \\ &\quad \left.\left(1+\sqrt{\frac{2\hbar\sqrt{\frac{0.93172\frac{(0.75)}{2}\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}}}{m_e c^2}}\right)+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\} \\ &= -31.63537\ eV - 0.12759\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \end{aligned} \tag{13.804}$$

From Eqs. (13.801-13.804), the total energy of $^{35}Cl_2$ is

$$E_{T+osc}\left({}^{35}Cl_2\right) = -31.63537\ eV + \bar{E}_{osc}\left({}^{35}Cl_2\right)$$
$$= -31.63537\ eV - 0.12759\ eV + \frac{1}{2}(0.06939\ eV) \quad (13.805)$$
$$= -31.72826\ eV$$

where the experimental ω_e (Eq. (13.791)) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The Cl_2 bond dissociation energy, $E_D\left({}^{35}Cl_2\right)$, is given by the difference between the total energies of the two $Cl3sp^3$ HOs and $E_{T+osc}\left({}^{35}Cl_2\right)$:

$$E_D\left({}^{35}Cl_2\right) = 2E_{Coulomb}\left(Cl,3sp^3\right) - E_{T+osc}\left({}^{35}Cl_2\right) \quad (13.806)$$

$E_{Coulomb}\left(Cl,3sp^3\right)$ is given by Eq. (13.759); thus, the ${}^{35}Cl_2$ bond dissociation energy, $E_D\left({}^{35}Cl_2\right)$, given by Eqs. (13.759) and (13.805-13.806) is

$$E_D\left({}^{35}Cl_2\right) = -2(14.60295\ eV) - E_{T+osc}\left({}^{35}Cl_2\right)$$
$$= -29.20590\ eV - (-31.72826\ eV) \quad (13.807)$$
$$= 2.52236\ eV$$

The experimental ${}^{35}Cl_2$ bond dissociation energy is [49]

$$E_D\left({}^{35}Cl_2\right) = 2.51412\ eV \quad (13.808)$$

The results of the determination of bond parameters of Cl_2 are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

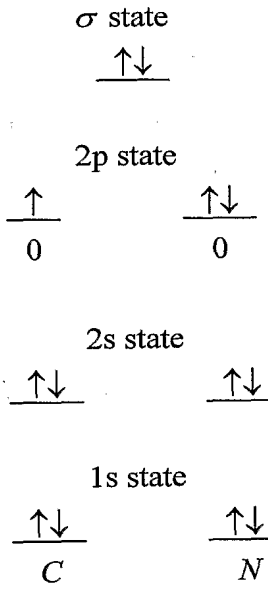
CARBON NITRIDE RADICAL

The carbon nitride radical can be formed by the reaction of carbon and nitrogen atoms:

$$C + N \rightarrow CN \quad (13.809)$$

The bond in carbon nitride radical comprises a H_2-type molecular orbital (MO) with two paired electrons. The force balance equations and radii, r_6 and r_7, of the $2p$ shell of C and N are derived in the Six-Electron Atoms section and Seven-Electron Atoms section, respectively. With the formation of the H_2-type MO by the contribution of a $2p$ electron from each of the C and N atoms, a diamagnetic force arises between the remaining $2p$ electrons of each atom and the H_2-type MO. This force from each atom causes the H_2-type

MO to move to greater principal axes than would result with the Coulombic force alone. But, the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $2p$ electrons of each atom decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of CN is $C1s^2N1s^2C2s^2N2s^2C2p^1N2p^2\sigma_{C,N}^2$ where σ designates the H_2-type MO, and the orbital arrangement is



(13.810)

The carbon nitride radical is predicted to be weakly paramagnetic .

FORCE BALANCE OF THE $2p$ SHELL OF THE CARBON ATOM OF THE CARBON NITRIDE RADICAL

For the C atom, force balance for the outermost $2p$ electron of CN (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Six-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of CN (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2}\mathbf{i}_r \tag{13.811}$$

for $r > r_4$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_5$.

The single unpaired carbon $2p$ electron gives rise to a diamagnetic force on the σ-MO as given by Eqs. (13.835-13.839). The corresponding Newtonian reaction force cancels $\mathbf{F}_{diamagnetic}$, of Eq. (10.82). The energy is minimized with conservation of angular momentum. This condition is met when

$$\mathbf{F}_{diamagnetic} = 0 \tag{13.812}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the maximum orbital angular momentum of the three $2p$ orbitals given by Eq. (10.89) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.813}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_5$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_5^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{13.814}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.811)) and diamagnetic (Eqs. (13.812) and (13.814)), and paramagnetic (Eq. (13.813)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \begin{pmatrix} \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{s(s+1)} \end{pmatrix} \tag{13.815}$$

Substitution of $v_5 = \frac{\hbar}{m_e r_5}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (13.815) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.816}$$

The quadratic equation corresponding to Eq. (13.816) is

$$r_5^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} + \frac{3\hbar^2}{Z m_e r_3}\sqrt{\frac{3}{4}}\right)} r_5 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} + \frac{3\hbar^2}{Z m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0$$

(13.817)

The solution of Eq. (13.817) using the quadratic formula is:

$$r_5 = \frac{\frac{a_0}{\left((Z-4)+\frac{3\sqrt{3}}{Z2r_3}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-4)+\frac{3\sqrt{3}}{Z2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-4)+\frac{3\sqrt{3}}{Z2r_3}\right)}}}{2} \qquad (13.818)$$

r_3 *in units of* a_0

The positive root of Eq. (13.818) must be taken in order that $r_5 > 0$. Substitution of $\frac{r_3}{a_0} = 0.84317$ (Eq. (10.62) with $Z = 6$) into Eq. (13.818) gives

$$r_5 = 0.88084 a_0 \qquad (13.819)$$

FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF THE CARBON NITRIDE RADICAL

For the N atom, force balance for the outermost $2p$ electron of CN (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$-shell as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of CN (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i}_r \qquad (13.820)$$

for $r > r_5$. The $2p$ shell possess an external electric field given by Eq. (10.92) for $r > r_6$.

The forces to determine the radius of the $N2p$ shell of N in CN are the same as those of N in N_2 except that in CN there is a contribution from the Newtonian reaction force that arises from the single unpaired carbon $2p$ electron. The energy is minimized with

conservation of angular momentum. This condition is met when $\mathbf{F}_{diamagnetic}$ of N in CN is canceled by the σ-MO -reaction force. Eq. (13.622) becomes

$$\mathbf{F}_{diamagnetic} = 0 \tag{13.821}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved orbital angular momentum of the three orbitals given by Eq. (10.89) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.822}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{13.823}$$

The N forces $\mathbf{F}_{ele}$, $\mathbf{F}_{mag\ 2}$, $\mathbf{F}_{diamagnetic\ 2}$, and $\mathbf{F}_{mag\ 3}$ of CN are the same as those of N_2 given by Eqs. (13.621) and (13.623-13.624), respectively. In both cases, the contribution of a $2p$ electron from the N atom in the formation of the σ MO gives rise to a paramagnetic force on the remaining two $2p$ electrons that pair. Thus, the force, $\mathbf{F}_{mag\ 3}$ of CN, given by Eq. (13.625) is

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.824}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.820)) and diamagnetic (Eqs. (13.821) and (13.823)), and paramagnetic (Eqs. (13.822) and (13.824)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left(\begin{array}{l}\frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} + \frac{3\hbar^2}{Z m_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\end{array}\right) \tag{13.825}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (13.626) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} + \frac{3\hbar^2}{Z m_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.826}$$

The quadratic equation corresponding to Eq. (13.826) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0}+\frac{3\hbar^2}{Zm_e r_3}\sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0}+\frac{3\hbar^2}{Zm_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.827}$$

The solution of Eq. (13.827) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-5)+\frac{3\sqrt{3}}{Z2r_3}\right)} \pm a_0 \sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)+\frac{3\sqrt{3}}{Z2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3\right)}{\left((Z-5)+\frac{3\sqrt{3}}{Z2r_3}\right)}}}{2} \tag{13.828}$$

r_3 *in units of* a_0

The positive root of Eq. (13.828) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (13.828) gives

$$r_6 = 0.76366 a_0 \tag{13.829}$$

ENERGIES OF THE $2p$ SHELLS OF THE CARBON AND NITROGEN ATOMS OF THE CARBON NITRIDE RADICAL

The central forces on the $2p$ shell of the C and N atoms are increased with the formation of the σ MO which reduces each shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the C and N atoms at the new radii are calculated and added to the energy of the σ MO to give the total energy of CN. Then, the bond energy is determined from the total CN energy.

The radius r_6 of the carbon atom before bonding is given by Eq. (10.122):

$$r_6 = 1.20654 a_0 \tag{13.830}$$

Using the initial radius r_6 of the C atom and the final radius r_5 of the $C2p$ shell of CN (Eq.

(13.819)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(CN,C2p)$ of the Coulombic energy change of the $C2p$ electron is determined using Eq. (10.102):

$$E_T(CN,C2p) = -\sum_{n=4}^{4} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_6}\right) = -(13.60580\ eV)(0.30647)(2) = -8.33948\ eV \quad (13.831)$$

The radius r_7 of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084 a_0 \quad (13.832)$$

Using the initial radius r_7 of the N atom and the final radius r_6 of the $N2p$ shell of CN (Eq. (13.829)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(CN,N2p)$ of the Coulombic energy change of the $N2p$ electron is determined using Eq. (10.102):

$$\begin{aligned} E_T(CN,N2p) &= -\sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_7}\right) \\ &= -(13.60580\ eV)(0.23518)(2+3) \\ &= -15.99929\ eV \end{aligned} \quad (13.833)$$

FORCE BALANCE OF THE σ MO OF THE CARBON NITRIDE RADICAL

The diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for the σ-MO of the CN molecule due to the two paired electrons in the $N2p$ shell given by Eq. (13.633) with $n_e = 2$ is:

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \quad (13.834)$$

The force $\mathbf{F}_{diamagneticMO2}$ is given by Eq. (13.634) except that the force is the summed over the individual diamagnetic-force terms due to each component of angular momentum $|L_i|$ acting on the electrons of the σ-MO from each atom having a nucleus of charge Z_j at one of the foci of the σ-MO:

$$\mathbf{F}_{diamagneticMO2} = \sum_{i,j} \frac{|L_i|\hbar}{Z_j 2m_e a^2 b^2} D\mathbf{i}_\xi \quad (13.835)$$

Using Eqs. (11.200), (13.633-13.634), and (13.834-13.835), the force balance for the σ-MO of the carbon nitride radical comprising carbon with charge $Z_1 = 6$ and $|L_1| = \hbar$ and

$|L_2| = \sqrt{\frac{3}{4}}\hbar$ and nitrogen with $Z_2 = 7$ and $|L_3| = \hbar$ is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.836}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D - \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.837}$$

$$\left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D \tag{13.838}$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) a_0 \tag{13.839}$$

Substitution of $Z_1 = 6$ and $Z_2 = 7$ into Eq. (13.839) gives

$$a = 2.45386 a_0 = 1.29853\ X\ 10^{-10}\ m \tag{13.840}$$

Substitution of Eq. (13.840) into Eq. (11.79) is

$$c' = 1.10767 a_0 = 5.86153\ X\ 10^{-11}\ m \tag{13.841}$$

The internuclear distance given by multiplying Eq. (13.841) by two is

$$2c' = 2.21534 a_0 = 1.17231\ X\ 10^{-10}\ m \tag{13.842}$$

The experimental bond distance from Ref. [28] is

$$2c' = 1.17181\ X\ 10^{-10}\ m \tag{13.843}$$

Substitution of Eqs. (13.840-13.841) into Eq. (11.80) is

$$b = c = 2.18964 a_0 = 1.15871\ X\ 10^{-10}\ m \tag{13.844}$$

Substitution of Eqs. (13.840-13.841) into Eq. (11.67) is

$$e = 0.45140 \tag{13.845}$$

Using the electron configuration of CN (Eq. (13.810), the radii of the $C1s = 0.17113 a_0$ (Eq. (10.51)), $C2s = 0.84317 a_0$ (Eq. (10.62)), $C2p = 0.88084 a_0$ (Eq. (13.819)), $N1s = 0.14605 a_0$ (Eq. (10.51)), $N2s = 0.69385 a_0$ (Eq. (10.62)), and $N2p = 0.76366 a_0$ (Eq. (13.829)) shells

and the parameters of the σ MO of CN given by Eqs. (13.3-13.4), (13.840-13.842), and (13.844-13.845), the dimensional diagram and charge-density of the CN MO are shown in Figures 27 and 28, respectively.

SUM OF THE ENERGIES OF THE σ MO AND THE AOs OF THE CARBON NITRIDE RADICAL

The energies of the CN σ MO are given by the substitution of the semiprincipal axes (Eqs. (13.840-13.841) and (13.844)) into the energy equations (Eqs. (11.207-11.212)) of H_2:

$$V_e = \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -23.90105\ eV \tag{13.846}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 12.28328\ eV \tag{13.847}$$

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 4.87009\ eV \tag{13.848}$$

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -2.43504\ eV \tag{13.849}$$

$$E_T = V_e + T + V_m + V_p \tag{13.850}$$

Substitution of Eqs. (11.79) and (13.846-13.849) into Eq. (13.850) gives

$$E_T(CN,\sigma) = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right) = -9.18273\ eV \tag{13.851}$$

where $E_T(CN,\sigma)$ is the total energy of the σ MO of CN. The sum, $E_T(CN)$, of $E_T(CN,C2p)$, the $C2p$ AO contribution given by Eq. (13.831), $E_T(CN,N2p)$, the $N2p$ AO contribution given by Eq. (13.833), and $E_T(CN,\sigma)$, the σ MO contribution given by Eq. (13.851) is:

$$\begin{aligned} E_T(CN) &= E_T(CN,C2p) + E_T(CN,N2p) + E_T(N_2,\sigma) \\ &= -8.33948\ eV - 15.99929\ eV - 9.18273\ eV \\ &= -33.52149\ eV \end{aligned} \tag{13.852}$$

VIBRATION OF *CN*

The vibrational energy levels of *CN* may be solved by determining the Morse potential curve from the energy relationships for the transition from a *C* atom and *N* atom whose parameters are given by Eqs. (10.115-10.123) and (10.134-10.143), respectively, to a *C* atom whose parameter r_5 is given by Eq. (10.819), a *N* atom whose parameter r_6 is given by Eq. (13.829), and the σ MO whose parameters are given by Eqs. (13.840-13.842) and (13.844-13.845). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF THE CARBON NITRIDE RADICAL

The equations of the radiation reaction force of *CN* are the same as those of H_2 with the substitution of the *CN* parameters. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 1.07550\,X\,10^{16}\ rad/s \tag{13.853}$$

where a is given by Eq. (13.840). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 1.07550\,X\,10^{16}\ rad/s = 7.07912\ eV \tag{13.854}$$

In Eq. (11.181), substitution of $E_T(CN)$ for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.854) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -33.59603\ eV\sqrt{\frac{2e(7.07912\ eV)}{m_e c^2}} = -0.17684\ eV \tag{13.855}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the *CN* MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation

of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.855) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental CN ω_e of 2068.59 cm^{-1} $(0.25647\ eV)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(CN)$ is

$$\overline{E}_{osc}(CN) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.856}$$

$$\overline{E}_{osc}(CN) = -0.17684\ eV + \frac{1}{2}(0.25647\ eV) = -0.04860\ eV \tag{13.857}$$

TOTAL AND BOND ENERGIES OF THE CARBON NITRIDE RADICAL

$E_{T+osc}(CN)$, the total energy of CN including the Doppler term, is given by the sum of $E_T(CN)$ (Eq. (13.852)) and $\overline{E}_{osc}(CN)$ given by Eq. (13.857):

$$\begin{aligned} E_{T+osc}(CN) &= V_e + T + V_m + V_p + E_T(CN, C2p) + E_T(CN, N2p) + \overline{E}_{osc}(CN) \\ &= E_T(CN, \sigma) + E_T(CN, C2p) + E_T(CN, N2p) + \overline{E}_{osc}(CN) \\ &= E_T(CN) + \overline{E}_{osc}(CN) \end{aligned} \tag{13.858}$$

$$E_{T+osc}(CN) = \left\{ \begin{array}{l} \left(\dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}} \left(\left(2 - \dfrac{1}{2}\dfrac{a_0}{a}\right) \ln \dfrac{a + \sqrt{\dfrac{aa_0}{2}}}{a - \sqrt{\dfrac{aa_0}{2}}} - 1 \right) \right. \\ \left. - \sum_{C,n=4}^{4} \dfrac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\dfrac{1}{r_5} - \dfrac{1}{r_6} \right) - \sum_{N,n=4}^{5} \dfrac{(Z-n)e^2}{8\pi\varepsilon_0} \left(\dfrac{1}{r_6} - \dfrac{1}{r_7} \right) \right) \\ \left(1 + \sqrt{\dfrac{2\hbar\sqrt{\dfrac{e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}} \right) + \dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}} \end{array} \right\} \tag{13.859}$$

$$= -33.52149\ eV - 0.17684\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

From Eqs. (13.856-13.859), the total energy of the CN MO is

$$\begin{aligned} E_{T+osc}(CN) &= -33.52149\ eV + \overline{E}_{osc}(CN) \\ &= -33.52149\ eV - 0.17684\ eV + \frac{1}{2}(0.25647\ eV) \\ &= -33.56970\ eV \end{aligned} \tag{13.860}$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The CN bond dissociation energy, $E_D(CN)$, is given by the difference between the sum of the energies of the C and N atoms and $E_{T+osc}(CN)$:

$$E_D(CN) = E(C) + E(N) - E_{T+osc}(CN) \tag{13.861}$$

where the energy of a carbon atom is [6]

$$E(C) = -11.26030\ eV \tag{13.862}$$

and the energy of a nitrogen atom is [6]

$$E(N) = -14.53414\ eV \tag{13.863}$$

Thus, the CN bond dissociation energy, $E_D(CN)$, given by Eqs. (13.860-13.863) is

$$\begin{aligned} E_D(CN) &= -(11.26030\ eV + 14.53414\ eV) - E_{T+osc}(CN) \\ &= -25.79444\ eV - (-33.56970\ eV) \\ &= 7.77526\ eV \end{aligned} \tag{13.864}$$

The experimental CN bond dissociation energy is [50]

$$E_{D298}(CN) = 7.7731\ eV \tag{13.865}$$

The results of the determination of bond parameters of CN are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

CARBON MONOXIDE MOLECULE

The carbon monoxide molecule can be formed by the reaction of carbon and oxygen atoms:

$$C + O \rightarrow CO \tag{13.866}$$

The bond in the carbon monoxide molecule comprises a double bond, a H_2-type molecular orbital (MO) with four paired electrons. The force balance equation and radius r_6 of the $2p$ shell of C is derived in the Six-Electron Atoms section. The force balance equation and radius r_8 of the $2p$ shell of O is derived in the Eight-Electron Atoms section. With the formation of the H_2-type MO by the contribution of two $2p$ electrons from each of the C and O atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the $2s$ electrons of C and the $2p$ electrons of O, and the H_2-type MO. This force from C

and O causes the H_2-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining $O2p$ electrons decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of CO is $C1s^2O1s^2C2s^2O2s^2O2p^2\sigma_{C,O}^4$ where σ designates the H_2-type MO, and the orbital arrangement is

σ state

$\uparrow\downarrow \quad \uparrow\downarrow$

2p state

$\uparrow\downarrow$

0

2s state

$\uparrow\downarrow \qquad \uparrow\downarrow$ (13.867)

1s state

$\uparrow\downarrow \qquad \uparrow\downarrow$

$C \qquad O$

Carbon monoxide is predicted to be diamagnetic in agreement with observations [42].

FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON MONOXIDE MOLECULE

For the O atom, force balance for the outermost $2p$ electron of CO (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$ electron as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of CO (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i}_r \tag{13.868}$$

for $r > r_5$. The $2p$ shell possess a +2 external electric field given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contribution is given by:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{13.869}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.870}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{13.871}$$

In addition, the contribution of two $2p$ electrons in the formation of the σ molecular orbital (MO) gives rise to a paramagnetic force on the remaining paired $2p$ electrons. The force $\mathbf{F}_{mag\ 3}$ is given by Eq. (13.625) wherein the radius is r_6 :

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.872}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.868)) and diamagnetic (Eqs. (13.869) and (13.871)), and paramagnetic (Eqs. (13.870) and (13.872)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \begin{pmatrix} \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)} \end{pmatrix} \tag{13.873}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (13.873) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}}$$

(13.874)

The quadratic equation corresponding to Eq. (13.874) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0}-\left(\frac{1}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0}-\left(\frac{1}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \qquad (13.875)$$

The solution of Eq. (13.875) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-5)-\left(\frac{1}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0 \sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)-\left(\frac{1}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3\right)}{\left((Z-5)-\left(\frac{1}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2} \qquad (13.876)$$

r_3 *in units of* a_0

The positive root of Eq. (13.876) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (13.876) gives

$$r_6 = 0.68835 a_0 \qquad (13.877)$$

ENERGIES OF THE $2s$ AND $2p$ SHELLS OF THE CARBON ATOM AND THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON MONOXIDE MOLECULE

With the formation of the H_2-type MO by the contribution of two $2p$ electrons from the C atom, the remaining outer-shell atomic electrons comprise the $2s$ electrons, which are unchanged by bonding with oxygen. However, the total energy of the CO molecule, which is subtracted from the sum of the energies of the carbon and oxygen atoms to determine the bond energy, is increased by the ionization energies of C^+ and O^+ given by Eqs. (10.113-10.114) and (10.152-10.153), respectively. Experimentally, the energies are [6]

$$E(ionization;\ C^+) = 24.38332\ eV \qquad (13.878)$$

$$E(ionization;\ O^+) = 35.11730\ eV \tag{13.879}$$

In addition, the central forces on the $2p$ shell of the O atom are increased with the formation of the σ MO, which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the O atom at the new radius are calculated and added to the ionization energies of C^+ and O^+, and the energy of the σ MO to give the total energy of CO. Then, the bond energy is determined from the total CO energy.

The radius r_8 of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \tag{13.880}$$

Using the initial radius r_8 of the O atom and the final radius r_6 of the $O2p$ shell (Eq. (13.877)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(O,2p)$ of the Coulombic energy change of the $O2p$ electrons of the O atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(O,2p) &= -\sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) \\ &= -(13.60580\ eV)(0.45275)(3+4) \\ &= -43.11996\ eV \end{aligned} \tag{13.881}$$

FORCE BALANCE OF THE σ MO OF THE CARBON MONOXIDE MOLECULE

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having $+2e$ at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having $+e$ at each focus. The diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for the σ-MO of the CO molecule due to the two paired electrons in each of the $C2s$ and $O2p$ shells is given by Eq. (13.633) with $n_e = 2$:

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.882}$$

The force $\mathbf{F}_{diamagneticMO2}$ is given by Eqs. (13.634) and (13.835) as the sum of the contributions due to carbon with $Z = Z_1$ and oxygen with $Z = Z_2$. $\mathbf{F}_{diamagneticMO1}$ for CO with $|L_i| = \hbar$ is

$$\mathbf{F}_{diamagneticMO2} = \left(\frac{1}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.883}$$

The force balance equation for the σ-MO of the carbon monoxide molecule given by Eqs. (11.200), (13.633-13.634), and (13.882-13.883) is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right)\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.884}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D - \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.885}$$

$$\left(2 + \frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D \tag{13.886}$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{1}{Z_2}\right) a_0 \tag{13.887}$$

Substitution of $Z_1 = 6$ and $Z_2 = 8$ into Eq. (13.887) gives

$$a = 2.29167 a_0 = 1.21270\, X\, 10^{-10}\ m \tag{13.888}$$

Substitution of Eq. (13.888) into Eq. (11.79) is

$$c' = 1.07044 a_0 = 5.66450\, X\, 10^{-11}\ m \tag{13.889}$$

The internuclear distance given by multiplying Eq. (13.889) by two is

$$2c' = 2.14087 a_0 = 1.13290\, X\, 10^{-10}\ m \tag{13.890}$$

The experimental bond distance is [28]

$$2c' = 1.12823\, X\, 10^{-10}\ m \tag{13.891}$$

Substitution of Eqs. (13.888-13.889) into Eq. (11.80) is

$$b = c = 2.02630 a_0 = 1.07227\, X\, 10^{-10}\ m \tag{13.892}$$

Substitution of Eqs. (13.888-13.889) into Eq. (11.67) is

$$e = 0.46710 \tag{13.893}$$

Using the electron configuration of CO (Eq. (13.867)), the radii of the $C1s = 0.17113 a_0$ (Eq. (10.51)), $C2s = 0.84317 a_0$ (Eq. (10.62)), $O1s = 0.12739 a_0$ (Eq. (10.51)), $O2s = 0.59020 a_0$ (Eq. (10.62)), and $O2p = 0.68835 a_0$ (Eq. (13.877)) shells and the parameters of the σ MO of CO given by Eqs. (13.3-13.4), (13.888-13.890), and (13.892-13.893), the dimensional diagram and charge-density of the CO MO are shown in Figures 29 and 30, respectively.

SUM OF THE ENERGIES OF THE σ MO AND THE AOs OF THE CARBON MONOXIDE MOLECULE

The energies of the CO σ MO are given by the substitution of the semiprincipal axes (Eqs. (13.888-13.889) and (13.892)) into the energy equations (Eqs. (11.207-11.212)) of H_2 except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the σ-MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -102.97635\ eV \tag{13.894}$$

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 50.84210\ eV \tag{13.895}$$

$$T = 2\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 11.23379\ eV \tag{13.896}$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -11.23379\ eV \tag{13.897}$$

$$E_T = V_e + T + V_m + V_p \tag{13.898}$$

Substitution of Eqs. (11.79) and (13.894-13.897) into Eq. (13.898) gives

$$E_T(CO,\sigma) = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 4\right) = -52.13425\ eV \tag{13.899}$$

where $E_T(CO,\sigma)$ is the total energy of the σ MO of CO. The total energy of CO, $E_T(CO)$, is given by the sum of $E(ionization;\ C^+)$, the energy of the second electron of carbon (Eq. (13.878)) donated to the double bond, $E(ionization;\ O^+)$, the energy of the second electron of oxygen (Eq. (13.879)) donated to the double bond, $E_T(O,2p)$, the $O2p$ AO contribution due to the decrease in radius with bond formation (Eq. (13.881)), and $E_T(CO,\sigma)$, the σ MO contribution given by Eq. (13.899):

$$\begin{aligned} E_T(CO) &= E(ionization;\ C^+) + E(ionization;\ O^+) + E_T(O,2p) + E_T(CO,\sigma) \\ &= 24.38332\ eV + 35.11730\ eV - 43.11996\ eV - 52.13425\ eV \\ &= -35.75359\ eV \end{aligned} \tag{13.900}$$

VIBRATION OF *CO*

The vibrational energy levels of CO may be solved by determining the Morse potential curve from the energy relationships for the transition from a C atom and O atom whose parameters are given by Eqs. (10.115-10.123) and (10.154-10.163), respectively, to a C atom whose parameter r_4 is given by Eq. (10.61), an O atom whose parameter r_6 is given by Eq. (13.877), and the σ MO whose parameters are given by Eqs. (13.888-13.890) and (13.892-13.893). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF THE CARBON MONOXIDE MOLECULE

The equations of the radiation reaction force of carbon monoxide are the same as those of H_2 with the substitution of the CO parameters except that there is a factor of four increase in the central force in Eq. (11.231) due to the double bond. Using Eqs. (11.231-11.233), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 2.38335\,X\,10^{16}\ rad/s \tag{13.901}$$

where a is given by Eq. (13.888). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.38335\,X\,10^{16}\ rad/s = 15.68762\ eV \tag{13.902}$$

In Eq. (11.181), substitution of $E_T(CO)$ for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.902) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -35.75359\ eV\sqrt{\frac{2e(15.68762\ eV)}{m_e c^2}} = -0.28016\ eV \tag{13.903}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the CO MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.903) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental CO ω_e of 2169.81 cm^{-1} $(0.26902\ eV)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}'_{osc}(CO)$ per bond is

$$\overline{E}'_{osc}(CO) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.904}$$

$$\overline{E}'_{osc}(CO) = -0.28016\ eV + \frac{1}{2}(0.26902\ eV) = -0.14564\ eV \tag{13.905}$$

Since the σ MO bond is a double bond with twice a many electrons as a single bond, $\overline{E}'_{osc}(CO)$ is multiplied by two to give

$$\overline{E}_{osc}(CO) = -0.29129\ eV \tag{13.906}$$

TOTAL AND BOND ENERGIES OF THE CARBON MONOXIDE MOLECULE

$E_{T+osc}(CO)$, the total energy of CO including the Doppler term, is given by the sum of $E_T(CO)$ (Eq. (13.900)) and $\overline{E}_{osc}(CO)$ given by Eq. (13.906):

$$\begin{aligned} E_{T+osc}(CO) &= \begin{pmatrix} V_e + T + V_m + V_p + E(ionization;\ C^+) \\ +E(ionization;\ O^+) + E_T(O,2p) + \overline{E}_{osc}(CO) \end{pmatrix} \\ &= \begin{pmatrix} E_T(CO,\sigma) + E(ionization;\ C^+) + E(ionization;\ O^+) \\ +E_T(O,2p) + \overline{E}_{osc}(CO) \end{pmatrix} \\ &= E_T(CO) + \overline{E}_{osc}(CO) \end{aligned} \tag{13.907}$$

$$E_{T+osc}(CO)=\left\{\begin{array}{l}\left(\begin{array}{l}\dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left(8\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-4\right)+E\left(ionization;\ C^+\right)\\ +E\left(ionization;\ O^+\right)-\sum\limits_{O,n=4}^{5}\dfrac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\dfrac{1}{r_6}-\dfrac{1}{r_8}\right)\end{array}\right)\\ \left(1+2\sqrt{\dfrac{2\hbar\sqrt{\dfrac{4e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right)+2\left(\dfrac{1}{2}\hbar\sqrt{\dfrac{k}{\mu}}\right)\end{array}\right\} \quad (13.908)$$

$$=-35.75359\ eV-2(0.28016\ eV)+2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

From Eqs. (13.906-13.908), the total energy of the CO MO is

$$\begin{aligned}E_{T+osc}(CO)&=-35.75359\ eV+\bar{E}_{osc}(CO)\\&=-35.75359\ eV+(-0.29129\ eV)\\&=-36.04488\ eV\end{aligned} \quad (13.909)$$

where the experimental ω_e was used for the $\hbar\sqrt{\dfrac{k}{\mu}}$ term.

The CO bond dissociation energy, $E_D(CO)$, is given by the difference between the sum of the energies of the C and O atoms and $E_{T+osc}(CO)$:

$$E_D(CO)=E(C)+E(O)-E_{T+osc}(CO) \quad (13.910)$$

where the energy of a carbon atom is [6]

$$E(C)=-11.26030\ eV \quad (13.911)$$

and the energy of an oxygen atom is [6]

$$E(O)=-13.61806\ eV \quad (13.912)$$

Thus, the CO bond dissociation energy, $E_D(CO)$, given by Eqs. (13.909-13.912) is

$$\begin{aligned}E_D(CO)&=-(11.26030\ eV+13.61806\ eV)-E_{T+osc}(CO)\\&=-24.87836\ eV-(-36.04488\ eV)\\&=11.16652\ eV\end{aligned} \quad (13.913)$$

The experimental CO bond dissociation energy is [49]

$$E_{D298}(CO)=11.15696\ eV \quad (13.914)$$

The results of the determination of bond parameters of CO are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

NITRIC OXIDE RADICAL

The nitric oxide radical can be formed by the reaction of nitrogen and oxygen atoms:

$$N + O \rightarrow NO \tag{13.915}$$

The bond in the nitric oxide radical comprises a double bond, a H_2-type molecular orbital (MO) with four paired electrons. The force balance equation and radius r_7 of the $2p$ shell of N is derived in the Seven-Electron Atoms section. The force balance equation and radius r_8 of the $2p$ shell of O is derived in the Eight-Electron Atoms section. With the formation of the H_2-type MO by the contribution of two $2p$ electrons from each of the N and O atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the $2s$ and $2p$ electrons of N and O, and the H_2-type MO. This force from N and O causes the H_2-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining N and O electrons decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of NO is $N1s^2O1s^2N2s^2O2s^2N2p^1O2p^2\sigma_{N,O}^4$ where σ designates the H_2-type MO, and the orbital arrangement is

σ state

$\underline{\uparrow\downarrow}\quad\underline{\uparrow\downarrow}$

2p state

$\underline{\uparrow}\qquad\underline{\uparrow\downarrow}$

0 0

2s state

$\underline{\uparrow\downarrow}\qquad\underline{\uparrow\downarrow}$

1s state

$\underline{\uparrow\downarrow}\qquad\underline{\uparrow\downarrow}$

$N\qquad O$

(13.916)

Nitric oxide is predicted to be weakly paramagnetic in agreement with observations [42].

FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF THE NITRIC OXIDE RADICAL

For the N atom, force balance for the outermost $2p$ electron of NO (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of NO (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2}\mathbf{i}_r \tag{13.917}$$

for $r > r_4$. The $2p$ shell possess a +2 external electric field given by Eq. (10.92) for $r > r_5$. The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of N in NO are the same as those of N in the nitrogen molecule with r_5 replacing r_6 and with an increase of the central field by an integer. The diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contribution is given by Eq. (13.622) with r_5 replacing r_6:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{\hbar^2}{12m_e r_5^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{13.918}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved orbital angular momentum of the three orbitals is

also the same as that of N_2 given by Eq. (13.623) with r_5 replacing r_6:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.919}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_5$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius follows from Eq. (13.624):

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_5^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{13.920}$$

In addition to the N forces $\mathbf{F}_{ele}$, $\mathbf{F}_{diamagnetic}$, $\mathbf{F}_{mag\ 2}$, and $\mathbf{F}_{diamagnetic\ 2}$ of NO being the same as N_2 given by Eqs. (13.621-13.624), respectively, $\mathbf{F}_{ele}$, $\mathbf{F}_{mag\ 2}$, and $\mathbf{F}_{diamagnetic\ 2}$ are also the same as those of CN (Eqs. (13.820) and (13.822-13.823)). In the N_2 and CN cases, the contribution of a $2p$ electron from the N atom in the formation of the σ MO gives rise to an additional paramagnetic force on the remaining two $2p$ electrons that pair. However, the force, $\mathbf{F}_{mag\ 3}$, is absent in NO since the single outer electron is unpaired.

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.917)) and diamagnetic (Eqs. (13.918) and (13.920)), and paramagnetic (Eq. (13.919)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \left(\begin{array}{l}\frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12 m_e r_5^2 r_3}\sqrt{s(s+1)} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{s(s+1)}\end{array}\right) \tag{13.921}$$

Substitution of $v_5 = \frac{\hbar}{m_e r_5}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (13.921) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12 m_e r_5^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{\frac{3}{4}} \tag{13.922}$$

The quadratic equation corresponding to Eq. (13.922) is

$$r_5^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_5 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{13.923}$$

The solution of Eq. (13.923) using the quadratic formula is:

$$r_5 = \frac{\frac{a_0}{\left((Z-4) - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-4) - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3\right)}{\left((Z-4) - \left(\frac{1}{12} - \frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2} \tag{13.924}$$

r_3 *in units of* a_0

The positive root of Eq. (13.924) must be taken in order that $r_5 > 0$. Substitution of $\frac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (13.924) gives

$$r_5 = 0.74841 a_0 \tag{13.925}$$

FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOM OF THE NITRIC OXIDE RADICAL

For the O atom, force balance for the outermost $2p$ electron of NO (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 6 and the other $2p$ electron as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of NO (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i}_r \tag{13.926}$$

for $r > r_5$. The $2p$ shell possess an external electric field of +2 given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contribution is given by:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{13.927}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eqs. (10.157) and (13.670) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.928}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{13.929}$$

In addition, the contribution of two $2p$ electrons in the formation of the σ MO gives rise to a paramagnetic force on the remaining paired $2p$ electrons. The force $\mathbf{F}_{mag\ 3}$ is given by Eq. (13.625) wherein the radius is r_6 :

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i}_r \tag{13.930}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (13.926)) and diamagnetic (Eqs. (13.927) and (13.929)), and paramagnetic (Eqs. (13.928) and (13.930)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left(\begin{array}{l}\frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\end{array}\right) \tag{13.931}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (13.931) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}}$$

(13.932)

The quadratic equation corresponding to Eq. (13.932) is

$$r_6^2-\frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0}-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)}r_6-\frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0}-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)}=0 \tag{13.933}$$

The solution of Eq. (13.933) using the quadratic formula is:

$$r_6=\frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\pm a_0\sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2+\frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2} \tag{13.934}$$

r_3 *in units of* a_0

The positive root of Eq. (13.934) must be taken in order that $r_6>0$. Substitution of $\frac{r_3}{a_0}=0.59020$ (Eq. (10.62) with $Z=8$) into Eq. (13.934) gives

$$r_6=0.70460a_0 \tag{13.935}$$

ENERGIES OF THE $2p$ SHELLS OF THE NITROGEN ATOM AND OXYGEN ATOM OF THE NITRIC OXIDE RADICAL

With the formation of the H_2-type MO by the contribution of two $2p$ electrons from each of the N and O atoms, the total energy of the NO molecule, which is subtracted from the sum of the energies of the nitrogen and oxygen atoms to determine the bond energy, is increased by the ionization energies of N^+ and O^+ given by Eqs. (10.132-10.133) and (10.152-10.153), respectively. Experimentally, the energies are [6]

$$E(ionization;\ N^+)=29.6013\ eV \tag{13.936}$$

$$E(ionization;\ O^+)=35.11730\ eV \tag{13.937}$$

In addition, the central forces on the $2p$ shells of the N and O atoms are increased

with the formation of the σ MO which reduces each shell's radius and increases its total energy. The Coulombic energy terms of the total energy of the N and O atoms at the new radii are calculated and added to the ionization energies of N^+ and O^+, and the energy of the σ MO to give the total energy of NO. Then, the bond energy is determined from the total NO energy.

The radius r_7 of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084 a_0 \tag{13.938}$$

Using the initial radius r_7 of the N atom and the final radius r_5 of the $N2p$ shell (Eq. (13.925)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(N,2p)$ of the Coulombic energy change of the $N2p$ electrons of the N atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(N,2p) &= -\sum_{n=4}^{4} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_7}\right) \\ &= -(13.60580\ eV)(0.26186)(3) \\ &= -10.68853\ eV \end{aligned} \tag{13.939}$$

The radius r_8 of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \tag{13.940}$$

Using the initial radius r_8 of the O atom and the final radius r_6 of the $O2p$ shell (Eq. (13.935)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(O,2p)$ of the Coulombic energy change of the $O2p$ electrons of the O atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(O,2p) &= -\sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) \\ &= -(13.60580\ eV)(0.41925)(3+4) \\ &= -39.92918\ eV \end{aligned} \tag{13.941}$$

FORCE BALANCE OF THE σ MO OF THE NITRIC OXIDE RADICAL

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having $+2e$ at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having $+e$ at each focus. The diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for the σ-MO of the NO molecule due to the two paired electrons in the $O2p$ shell is given by

Eq. (13.633) with $n_e = 2$:

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.942}$$

$\mathbf{F}_{diamagneticMO2}$ of the nitric oxide radical comprising nitrogen with charge $Z_1 = 7$ and $|L_1| = \hbar$ and $|L_2| = \sqrt{\frac{3}{4}}\hbar$ and oxygen with $Z_2 = 8$ and $|L_3| = \hbar$ is given by the corresponding sum of the contributions. Using Eq. (13.835), $\mathbf{F}_{diamagneticMO2}$ for NO is

$$\mathbf{F}_{diamagneticMO2} = \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{13.943}$$

The general force balance equation for the σ-MO of the nitric oxide radical given by Eqs. (11.200), (13.633-13.634), and (13.942-13.943) is the same as that of CN (Eq. (13.836)):

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.944}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D - \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D \tag{13.945}$$

$$\left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D \tag{13.946}$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) a_0 \tag{13.947}$$

Substitution of $Z_1 = 7$ and $Z_2 = 8$ into Eq. (13.947) gives

$$a = 2.39158 a_0 = 1.26557\, X\, 10^{-10}\ m \tag{13.948}$$

Substitution of Eq. (13.948) into Eq. (11.79) is

$$c' = 1.09352 a_0 = 5.78666\, X\, 10^{-11}\ m \tag{13.949}$$

The internuclear distance given by multiplying Eq. (13.949) by two is

$$2c' = 2.18704a_0 = 1.15733\,X\,10^{-10}\ m \tag{13.950}$$

The experimental bond distance is [28]

$$2c' = 1.15077\,X\,10^{-10}\ m \tag{13.951}$$

Substitution of Eqs. (13.948-13.949) into Eq. (11.80) is

$$b = c = 2.12693a_0 = 1.12552\,X\,10^{-10}\ m \tag{13.952}$$

Substitution of Eqs. (13.948-13.949) into Eq. (11.67) is

$$e = 0.45724 \tag{13.953}$$

Using the electron configuration of NO (Eq. (13.916)), the radii of the $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), $N2p = 0.74841a_0$ (Eq. (13.925)), $O1s = 0.12739a_0$ (Eq. (10.51)), $O2s = 0.59020a_0$ (Eq. (10.62)), and $O2p = 0.70460a_0$ (Eq. (13.935)) shells and the parameters of the σ MO of NO given by Eqs. (13.3-13.4), (13.948-13.950), and (13.952-13.953), the dimensional diagram and charge-density of the NO MO are shown in Figures 31 and 32, respectively.

SUM OF THE ENERGIES OF THE σ MO AND THE AOs OF THE NITRIC OXIDE RADICAL

The energies of the NO σ MO are given by the substitution of the semiprincipal axes (Eqs. (13.948-13.949) and (13.952)) into the energy equations (Eqs. (11.207-11.212)) of H_2 except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the σ-MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -98.30623\ eV \tag{13.954}$$

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 49.76880\ eV \tag{13.955}$$

$$T = 2\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 10.27631\ eV \tag{13.956}$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.27631\ eV \tag{13.957}$$

$$E_T = V_e + T + V_m + V_p \tag{13.958}$$

Substitution of Eqs. (11.79) and (13.954-13.957) into Eq. (13.958) gives

$$E_T(NO,\sigma)=\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-4\right)=-48.53743\ eV \tag{13.959}$$

where $E_T(NO,\sigma)$ is the total energy of the σ MO of NO. The total energy of NO, $E_T(NO)$, is given by the sum of $E(ionization;\ N^+)$, the energy of the second electron of nitrogen (Eq. (13.936)) donated to the double bond, $E(ionization;\ O^+)$, the energy of the second electron of oxygen (Eq. (13.937)) donated to the double bond, $E_T(N,2p)$, the $N2p$ AO contribution due to the decrease in radius with bond formation (Eq. (13.939)), $E_T(O,2p)$, the $O2p$ AO contribution due to the decrease in radius with bond formation (Eq. (13.941)), and $E_T(NO,\sigma)$, the σ MO contribution given by Eq. (13.959):

$$\begin{aligned}E_T(NO)&=\begin{pmatrix}E(ionization;\ N^+)+E(ionization;\ O^+)\\+E_T(N,2p)+E_T(O,2p)+E_T(NO,\sigma)\end{pmatrix}\\&=\begin{pmatrix}29.6013\ eV+35.11730\ eV\\-10.68853\ eV-39.92918\ eV-48.53743\ eV\end{pmatrix}\\&=-34.43653\ eV\end{aligned} \tag{13.960}$$

VIBRATION OF *NO*

The vibrational energy levels of NO may be solved by determining the Morse potential curve from the energy relationships for the transition from a N atom and O atom whose parameters are given by Eqs. (10.134-10.143) and (10.154-10.163), respectively, to a N atom whose parameter r_5 is given by Eq. (13.925), an O atom whose parameter r_6 is given by Eq. (13.935), and the σ MO whose parameters are given by Eqs. (13.948-13.950) and (13.952.-13.953). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [15] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF THE NITRIC OXIDE RADICAL

The equations of the radiation reaction force of nitric oxide are the same as those of H_2 with the substitution of the NO parameters except that there is a factor of four increase in the central force in Eq. (11.231) due to the double bond. Using Eqs. (11.231-11.233) and (13.901), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 2.23557\,X\,10^{16}\ rad/s \tag{13.961}$$

where a is given by Eq. (13.948). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.23557\,X\,10^{16}\ rad/s = 14.71493\ eV \tag{13.962}$$

In Eq. (11.181), substitution of $E_T(NO)$ for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (13.962) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -34.43653\ eV\sqrt{\frac{2e(14.71493\ eV)}{m_e c^2}} = -0.26134\ eV \tag{13.963}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the NO MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (13.963) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy. Using the experimental NO ω_e of 1904.20 cm^{-1} $(0.23609\ eV)$ [28] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}'_{osc}(NO)$ per bond is

$$\overline{E}'_{osc}(NO) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{13.964}$$

$$\overline{E}'_{osc}(NO) = -0.26134\ eV + \frac{1}{2}(0.23609\ eV) = -0.14329\ eV \tag{13.965}$$

Since the σ MO bond is a double bond with twice a many electrons as a single bond, $\overline{E}'_{osc}(NO)$ is multiplied by two to give

$$\overline{E}_{osc}(NO) = -0.28658\ eV \tag{13.966}$$

TOTAL AND BOND ENERGIES OF THE NITRIC OXIDE RADICAL

$E_{T+osc}(NO)$, the total energy of NO including the Doppler term, is given by the sum of $E_T(NO)$ (Eq. (13.960)) and $\bar{E}_{osc}(NO)$ given by Eq. (13.966):

$$\begin{aligned} E_{T+osc}(NO) &= \begin{pmatrix} V_e + T + V_m + V_p + E(ionization;\ N^+) + E(ionization;\ O^+) \\ + E_T(N,2p) + E_T(O,2p) + \bar{E}_{osc}(NO) \end{pmatrix} \\ &= \begin{pmatrix} E_T(NO,\sigma) + E(ionization;\ N^+) + E(ionization;\ O^+) \\ + E_T(N,2p) + E_T(O,2p) + \bar{E}_{osc}(NO) \end{pmatrix} \\ &= E_T(NO) + \bar{E}_{osc}(NO) \end{aligned} \tag{13.967}$$

$$\begin{aligned} E_{T+osc}(NO) = \Bigg\{ & \Bigg(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 4 \right) \\ & + E(ionization;\ N^+) + E(ionization;\ O^+) \\ & - \sum_{N,n=4}^{4} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_7}\right) - \sum_{O,n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) \Bigg) \Bigg\} \\ & \left(1 + 2\sqrt{\frac{2\hbar\sqrt{\frac{4e^2}{4\pi\varepsilon_o a^3 m_e}}}{m_e c^2}} \right) + 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \\ = & -34.43653\ eV - 2(0.26134\ eV) + 2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \end{aligned} \tag{13.968}$$

From Eqs. (13.966-13.968), the total energy of the NO MO is

$$\begin{aligned} E_{T+osc}(NO) &= -34.43653\ eV + \bar{E}_{osc}(NO) \\ &= -34.43653\ eV + (-0.28658) \\ &= -34.72312\ eV \end{aligned} \tag{13.969}$$

where the experimental ω_e was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The NO bond dissociation energy, $E_D(NO)$, is given by the difference between the sum of the energies of the N and O atoms and $E_{T+osc}(NO)$:

$$E_D(NO) = E(N) + E(O) - E_{T+osc}(NO) \tag{13.970}$$

where the energy of a nitrogen atom is [6]

$$E(N) = -14.53414\ eV \tag{13.871}$$

and the energy of an oxygen atom is [6]

$$E(O) = -13.61806\ eV \tag{13.972}$$

Thus, the NO bond dissociation energy, $E_D(NO)$, given by Eqs. (13.969-13.972) is

$$\begin{aligned} E_D(NO) &= -(14.53414\ eV + 13.61806\ eV) - E_{T+osc}(NO) \\ &= -28.15220\ eV - (-34.72312\ eV) \\ &= 6.57092\ eV \end{aligned} \tag{13.973}$$

The experimental NO bond dissociation energy is [49]

$$E_{D298}(NO) = 6.5353\ eV \tag{13.974}$$

The results of the determination of bond parameters of NO are given in Table 13.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Table 13.1. The calculated and experimental bond parameters of H_3^+, D_3^+, OH, OD, H_2O, D_2O, NH, ND, NH_2, ND_2, NH_3, ND_3, CH, CD, CH_2, CH_3, CH_4, N_2, O_2, F_2, Cl_2, CN, CO, and NO.

Parameter	Calculated	Experimental	Ref. for Exp.
H_3^+ Bond Energy	4.373 eV	4.373 eV	8
D_3^+ Bond Energy	4.374 eV		
OH Bond Energy	4.4104 eV	4.4117 eV	22
OD Bond Energy	4.4687 eV	4.454 eV	23
OH Bond Length	0.971651 Å	0.971 Å	13
OD Bond Length	0.971651 Å	0.971 Å	13
OH Vibrational Energy	0.4367 eV	0.4424 eV	16-17
OD Vibrational Energy	0.3219 eV	0.3263 eV	16-17
OH ω_e	3696.38 cm^{-1}	3735.21 cm^{-1}	14
OD ω_e	2689.51 cm^{-1}	2720.9 cm^{-1}	14
OH $\omega_e x_e$	87.18 cm^{-1}	82.81 cm^{-1}	14
OD $\omega_e x_e$	46.75 cm^{-1}	44.2 cm^{-1}	14
OH B_e	18.835 cm^{-1}	18.871 cm^{-1}	14

Parameter	Calculated	Experimental	Ref. for Exp.
OD B_e	9.971 cm^{-1}	10.01 cm^{-1}	14
H_2O Bond Energy	5.1059 eV	5.0991 eV	26
D_2O Bond Energy	5.178 eV	5.191 eV	31-32
H_2O $O-H$ Bond Length	0.971574 Å	0.970 ± 0.005 Å	23
D_2O $O-D$ Bond Length	0.971574 Å	0.970 ± 0.005 Å	23
H_2O $H-H$ Distance	1.552 Å	1.55 ± 0.01 Å	13
D_2O $D-D$ Distance	1.552 Å	1.55 ± 0.01 Å	13
H_2O Bond Angle	106°	106°	23
D_2O Bond Angle	106°	106°	23
NH Bond Energy	3.47530 eV	3.47 eV	30
ND Bond Energy	3.52556 eV	3.5134 eV	31
NH Bond Length	1.04262 Å	1.0362 Å	28
ND Bond Length	1.04262 Å	1.0361 Å	28
NH Vibrational Energy	0.38581 eV	0.38752 eV	28
ND Vibrational Energy	0.28583 eV	0.28690 eV	28
NH ω_e	3284.58 cm^{-1}	3282.3 cm^{-1}	28
ND ω_e	2398.72 cm^{-1}	2398 cm^{-1}	28
NH $\omega_e x_e$	86.37 cm^{-1}	78.4 cm^{-1}	28
ND $\omega_e x_e$	47.40 cm^{-1}	42 cm^{-1}	28
NH B_e	16.495 cm^{-1}	16.993 cm^{-1}	28
ND B_e	8.797 cm^{-1}	8.7913 cm^{-1}	28
NH_2 Bond Energy	3.9323 eV	3.9461 eV	35
ND_2 Bond Energy	3.9401 eV	3.9362 eV	33-35
NH_2 Bond Length	1.04262 Å	1.0240 Å	32
ND_2 Bond Length	1.04262 Å		
NH_2 Bond Angle	105.97	103.3°	32
ND_2 Bond Angle	105.97		
NH_3 Bond Energy	4.57913 eV	4.60155 eV	37
ND_3 Bond Energy	4.64499 eV	4.71252 eV	37

Parameter	Calculated	Experimental	Ref. for Exp.
NH_3 Bond Length	1.0368 Å	1.012 Å	32
ND_3 Bond Length	1.0368 Å		
NH_3 Bond Angle	106.67	106.67°	36
ND_3 Bond Angle	106.67	106.70	36
CH Bond Energy	3.47404 eV	3.47 eV	14
CD Bond Energy	3.51673 eV	3.52 eV	14
CH Bond Length	1.1183 Å	1.1198 Å	14
CD Bond Length	1.1183 Å	1.118 Å	14
CH Vibrational Energy	0.33879 eV	0.33885 eV	14
CD Vibrational Energy	0.25173 eV	0.25189 eV	14
CH ω_e	2865.86 cm^{-1}	2861.6 cm^{-1}	14
CD ω_e	2102.97 cm^{-1}	2101.0 cm^{-1}	14
CH $\omega_e x_e$	66.624 cm^{-1}	64.3 cm^{-1}	14
CD $\omega_e x_e$	36.335 cm^{-1}	34.7 cm^{-1}	14
CH B_e	14.498 cm^{-1}	14.457 cm^{-1}	14
CD B_e	7.807 cm^{-1}	7.808 cm^{-1}	14
CH_2 Bond Energy	4.36968 eV	4.33064 eV	39
CH_2 Bond Length	1.1067 Å	1.111 Å	38
CH_2 Bond Angle	100.22	102.4°	38
CH_3 Bond Energy	4.70075 eV	4.72444 eV	40
CH_3 Bond Length	1.1029 Å	1.079 Å	38
CH_3 Bond Angle	100.70°		
CH_4 Bond Energy	4.4900 eV	4.48464 eV	40
CH_4 Bond Length	1.1010 Å	1.087 Å	41
CH_4 Bond Angle	109.5°	109.5°	41
N_2 Bond Energy	9.71181 eV	9.756 eV	43
N_2 Bond Length	1.0955 Å	1.094 Å	43
O_2 Bond Energy	5.10711 eV	5.11665 eV	46
O_2 Bond Length	1.20862 Å	1.20752 Å	28

Parameter	Calculated	Experimental	Ref. for Exp.
F_2 Bond Energy	1.62168 eV	1.606 eV	48
F_2 Bond Length	1.41114 Å	1.41193 Å	28
Cl_2 Bond Energy	2.52236 eV	2.51412 eV	49
Cl_2 Bond Length	1.988 Å	1.988 Å	28
Cl_2 ω_e	538.52 cm^{-1}	559.7 cm^{-1}	28
Cl_2 $\omega_e x_e$	3.41 cm^{-1}	2.68 cm^{-1}	28
Cl_2 B_e	0.2420 cm^{-1}	0.2440 cm^{-1}	28
CN Bond Energy	7.77526 eV	7.7731 eV	50
CN Bond Length	1.17231 Å	1.17181 Å	28
CO Bond Energy	11.16652 eV	11.15696 eV	49
CO Bond Length	1.13290 Å	1.12823 Å	28
NO Bond Energy	6.57092 eV	6.5353 eV	49
NO Bond Length	1.15733 Å	1.15077 Å	28

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Section III

MORE POLYATOMIC MOLECULES AND HYDROCARBONS

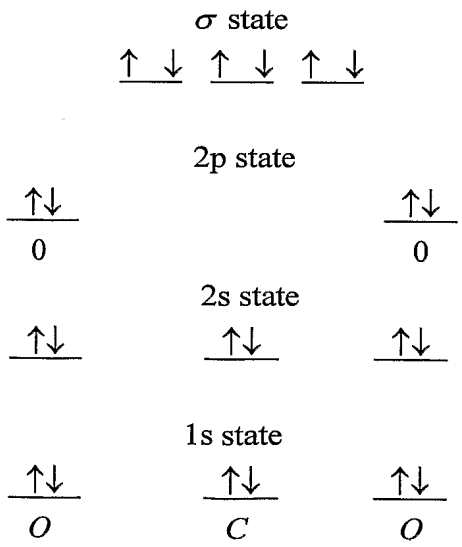
Additional polyatomic molecules can be solved using the same principles as those used to solve hydrogen molecular ions and molecules wherein the hydrogen molecular orbitals (MOs) and hydrogen atomic orbitals serve as basis functions for the MOs. The MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of $\hbar$. Energy of the MO must be matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the AO. Alternatively, the MO is continuous with the AO containing paired electrons that do not particpate in the bond. Rather, they only provide a means for the energy matched MO to form a continuous equipotential energy surface. In the case that an independent MO is formed, the AO force balance causes the remaining electrons to be at lower energy and a smaller radius. In another case, the atomic orbital may hybridize in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. Representative cases were solved. Specifically, the results of the determination of bond parameters of carbon dioxide (CO_2), nitrogen dioxide (NO_2), ethane (CH_3CH_3), ethylene (CH_2CH_2), acetylene ($CHCH$), benzene (C_6H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}), nonane (C_9H_{20}), decane ($C_{10}H_{22}$), undecane ($C_{11}H_{24}$), dodecane ($C_{12}H_{26}$), and octadecane ($C_{18}H_{38}$) are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

CARBON DIOXIDE MOLECULE

The carbon dioxide molecule can be formed by the reaction of carbon monoxide and an oxygen atom:

$$CO + O \rightarrow CO_2 \tag{14.1}$$

Each equivalent bond in the carbon dioxide molecule comprises a double bond that is energy-matched to the filled $C2s$ orbital. Each such bond comprises 75% of a H_2-type MO with four paired electrons as a basis set such that three electrons can be assigned to each $C=O$ bond. Thus, the two $C2p$ electrons combine with the four $O2p$ electrons, two from each O, as a linear combination to form the two $C=O$ bonds of CO_2. The force balance equation and radius r_8 of the $2p$ shell of O is derived in the Eight-Electron Atoms section. With the formation of the H_2-type MOs by the contribution of two $2p$ electrons from each of the two O atoms, a factor of two increase of the central field on the remaining $O2p$ electrons arises. The resulting increased Coulombic as well as magnetic central forces decrease the radii of the $O2p$ shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of CO_2 is $C1s^2O_1 1s^2O_2 1s^2C2s^2O_1 2s^2O_2 2s^2O_1 2p^2O_2 2p^2\sigma^6_{O_2,C,O_1}$ where the subscripts designate the O atom, 1 or 2, σ designates the H_2-type MO, and the orbital arrangement is



(14.2)

Carbon dioxide is predicted to be diamagnetic in agreement with observations [1].

FORCE BALANCE OF THE $2p$ SHELL OF THE OXYGEN ATOM OF THE CARBON DIOXIDE MOLECULE

For each O atom, force balance for the outermost $2p$ electron of CO_2 (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due

to interactions between electron 6 and the other $2p$ electrons as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of CO (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i}_r \tag{14.3}$$

for $r > r_5$. The $2p$ shell possess a +2 external electric field given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contribution is given by:

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{14.4}$$

where $s = 1/2$. And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eq. (10.157) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{14.5}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is :

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{14.6}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.3)) and diamagnetic (Eqs. (14.4) and (14.6)), and paramagnetic (Eq. (14.5)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{s(s+1)} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} \tag{14.7}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (14.7) gives:

$$\frac{\hbar^2}{m_e r_6^3}=\frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}-\frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}+\frac{2\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}}-\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{14.8}$$

The quadratic equation corresponding to Eq. (14.8) is

$$r_6^2-\frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0}-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)}r_6-\frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0}-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)}=0 \tag{14.9}$$

The solution of Eq. (14.9) using the quadratic formula is:

$$r_6=\frac{\frac{a_0}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\pm a_0\sqrt{\left(\frac{1}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2+\frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2} \tag{14.10}$$

r_3 *in units of* a_0

The positive root of Eq. (14.10) must be taken in order that $r_6>0$. Substitution of $\frac{r_3}{a_0}=0.59020$ (Eq. (10.62) with $Z=8$) into Eq. (14.10) gives

$$r_6=0.74776a_0 \tag{14.11}$$

ENERGIES OF THE $2s$ AND $2p$ SHELLS OF THE CARBON ATOM AND THE $2p$ SHELL OF THE OXYGEN ATOMS OF THE CARBON DIOXIDE MOLECULE

Consider the determination of the total energy of CO_2 from the reaction of a carbon atom with two oxygen atoms. With the formation of the H_2-type MO by the contribution of two $2p$ electrons from the C atom, the remaining outer-shell atomic electrons comprise the $2s$ electrons which are unchanged by bonding with two oxygen atoms. However, the total energy of the CO_2 molecule, which is subtracted from the sum of the energies of the oxygen atom and carbon monoxide molecule to determine the $O-CO$ bond energy, is increased by

the ionization energies of C, C^+, O, and $2O^+$ given by Eqs. (14.12-14.15), respectively. Experimentally, the energies are [2]

$$E(ionization;\ C) = 11.26030\ eV \tag{14.12}$$

$$E(ionization;\ C^+) = 24.38332\ eV \tag{14.13}$$

$$E(ionization;\ O) = 13.61806\ eV \tag{14.14}$$

$$E(ionization;\ O^+) = 35.11730\ eV \tag{14.15}$$

In addition, the central forces on the $2p$ shell of the O atom are increased with the formation of the σ MO which reduces the shell's radius and increases its total energy. The Coulombic energy terms of the total energy of each O atom at the new radius are calculated and added to the ionization energies of C, C^+, O, and $2O^+$, and the energy of the σ MO to give the total energy of CO_2. Then, the bond energy is determined from the total CO_2 energy.

The radius r_8 of each oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \tag{14.16}$$

Using the initial radius r_8 of each O atom and the final radius r_6 of the $O2p$ shell (Eq. (14.11)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(O,2p)$ of the Coulombic energy change of the $O2p$ electrons of each O atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(O,2p) &= -\sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) \\ &= -(13.60580\ eV)(0.33733)(3+4) \\ &= -32.12759\ eV \end{aligned} \tag{14.17}$$

FORCE BALANCE OF THE σ MO OF THE CARBON DIOXIDE MOLECULE

As in the case of H_2, the σ MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into the C atom for distances shorter than the radius of the $C2s$ shell; nor, can it extend into the O atom for distances shorter than the radius of the $O2p$ shell. Thus, the MO surface of each $C=O$ bond comprises a prolate spheroid that bridges and is continuous with the $2s$ and $2p$ shells of the O and C atoms whose nuclei serve as the foci. The energy of each prolate spheroid is matched to that of the $C2s$ and $O2p$ shells.

As in the case of previous examples of energy-matched MOs such as OH and NH, the $C=O$-bond MO must comprise 75% of a H_2-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. However, the paired electrons of the $C2s$ and $O2p$ shells are not involved in bonding. Rather, the AOs permit a continuous surface comprising the two $C=O$-bond MOs having six paired electrons, two from each of the C and the two O atoms:

$$2(0.75\ H_2\ MO) \rightarrow CO_2\ MO \tag{14.18}$$

The force balance of the CO_2 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.18) and the energy matching condition between the carbon and oxygen components of the MO.

Similar to the OH and H_2O cases given by Eqs. (13.57) and (13.162), the H_2-type ellipsoidal MO comprises 75% of the CO_2 MO; so, the electron charge density in Eq. (11.65) is given by $-0.75e$. Thus, k' of the each H_2-type-ellipsoidal-MO component of the CO_2 MO is given by Eq. (13.59). The distance from the origin of each $C=O$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C=O$-bond MO $b=c$ given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). Then, the solution of the semimajor axis a allows for the solution of the other axes of the prolate spheroidal and eccentricity of the CO_2 MO.

The energy components of V_e, V_p, T, V_m, and E_T of the CO_2 σ MO are the same as those of OH given by Eqs. (13.67-13.73), except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to each σ-MO double bond:

$$E_T(C=O,\sigma) = -\frac{4e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}\right)\ln\frac{a+c'}{a-c'} - 1\right] \tag{14.19}$$

where $E_T(C=O,\sigma)$ is the total energy of each $C=O$ σ MO of CO_2. The total energy of a H_2-type ellipsoidal MO is given by Eqs. (11.212) and (13.75). A minimum energy is obtained when each double bond of the σ MO of CO_2 comprises the energy equivalent of four H_2-type ellipsoidal MOs. For each $C=O$ bond to match the energy of the $C2s$ orbital,

the ionization energy of C and C^+ (Eqs. (14.12-14.13)) must be added for each bond of the double bond. Thus, the total energy of each $C=O$-bond MOs is

$$\begin{aligned} E_T(C=O,\sigma) &= 2\left(\begin{array}{l} 2\left(-\frac{e^2}{8\pi\varepsilon_0 a_0}\left[\left(2\sqrt{2}-\sqrt{2}+\frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1}-\sqrt{2}\right]\right) \\ +E(ionization;\ C)+E(ionization;\ C^+) \end{array}\right) \\ &= 2\left(2\left(-31.63536831\ eV\right)+11.26030\ eV+24.38332\ eV\right) \\ &= -55.25423\ eV \end{aligned} \tag{14.20}$$

$E_T(C=O,\sigma)$ given by Eq. (14.19) is set equal to Eq. (14.20):

$$\frac{4e^2}{8\pi\varepsilon_0 c'}\left[\left(\frac{3}{2}\right)\ln\frac{a+c'}{a-c'}-1\right]=e55.25423\ eV \tag{14.21}$$

From the energy relationship given by Eq. (14.21) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CO_2 MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.21) gives

$$E_T(C=O,\sigma)=\frac{4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e55.25423\ eV \tag{14.22}$$

The most convenient way to solve Eq. (14.22) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.80703a_0=9.56239\ X\ 10^{-11}\ m \tag{14.23}$$

Substitution of Eq. (14.23) into Eq. (13.60) is

$$c'=1.09758a_0=5.80815\ X\ 10^{-11}\ m \tag{14.24}$$

The internuclear distance given by multiplying Eq. (14.24) by two is

$$2c'=2.19516a_0=1.16163\ X\ 10^{-10}\ m \tag{14.25}$$

The experimental bond distance is [3]

$$2c'=1.1600\ X\ 10^{-10}\ m \tag{14.26}$$

Substitution of Eqs. (14.23-14.24) into Eq. (13.62) is

$$b=c=1.43550a_0=7.59636\ X\ 10^{-11}\ m \tag{14.27}$$

Substitution of Eqs. (14.23-14.24) into Eq. (13.63) is

$$e=0.60740 \tag{14.28}$$

The C and O nuclei comprise the foci of each H_2-type ellipsoidal MO defined as $O=C=O$. Consider the left-hand $C=O$ bond of the two equivalent bonds in the absence

of the right-hand bond. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C2s$ AO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_4 = 0.84317a_0$ is the radius of the $C2s$ shell. Substitution of Eqs. (14.23-14.24) into Eq. (13.261) gives

$$\theta' = 54.53° \tag{14.29}$$

Then, the angle θ_{C2sAO} the radial vector of the $C2s$ AO makes with the internuclear axis is

$$\theta_{C2sAO} = 180° - 54.53° = 125.47° \tag{14.30}$$

as shown in Figure 33. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C2s$ radial vector obeys the following relationship:

$$r_4 \sin\theta_{C2sAO} = 0.84317a_0 \sin\theta_{C2sAO} = b \sin\theta_{H_2MO} \tag{14.31}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.84317a_0 \sin\theta_{C2sAO}}{b} = \sin^{-1}\frac{0.84317a_0 \sin 125.47°}{b} \tag{14.32}$$

with the use of Eq. (14.30). Substitution of Eq. (14.27) into Eq. (14.32) gives

$$\theta_{H_2MO} = 28.58° \tag{14.33}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{14.34}$$

Substitution of Eqs. (14.23) and (14.33) into Eq. (14.34) gives

$$d_{H_2MO} = 1.58687a_0 = 8.39737\,X\,10^{-11}\ m \tag{14.35}$$

The distance d_{C2sAO} along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C2sAO} = d_{H_2MO} - c' \tag{14.36}$$

Substitution of Eqs. (14.24) and (14.35) into Eq. (14.36) gives

$$d_{C2sAO} = 0.48929a_0 = 2.58922\,X\,10^{-11}\ m \tag{14.37}$$

The C and O nuclei comprise the foci of each H_2-type ellipsoidal MO defined as $O=C=O$. Consider the right-hand $C=O$ bond of the two equivalent bonds. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $O2p$ AO are

given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_6 = 0.74776a_0$ is the radius of the $O2p$ shell. Substitution of Eqs. (14.23-14.24) into Eq. (13.261) gives

$$\theta' = 30.18° \tag{14.38}$$

Then, the angle θ_{O2pAO} the radial vector of the $O2p$ AO makes with the internuclear axis is

$$\theta_{O2pAO} = 180° - 30.18° = 149.82° \tag{14.39}$$

as shown in Figure 33. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $O2p$ radial vector obeys the following relationship:

$$r_6 \sin\theta_{O2pAO} = 0.74776a_0 \sin\theta_{O2pAO} = b\sin\theta_{H_2MO} \tag{14.40}$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{0.74776a_0 \sin\theta_{O2pAO}}{b} = \sin^{-1}\frac{0.74776a_0 \sin 149.82°}{b} \tag{14.41}$$

with the use of Eq. (14.39). Substitution of Eq. (14.27) into Eq. (14.41) gives

$$\theta_{H_2MO} = 15.18° \tag{14.42}$$

Then, the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{14.43}$$

Substitution of Eqs. (14.23) and (14.42) into Eq. (14.43) gives

$$d_{H_2MO} = 1.74396a_0 = 9.22862\,X\,10^{-11}\ m \tag{14.44}$$

The distance d_{O2pAO} along the internuclear axis from the origin of each O atom to the point of intersection of the orbitals is given by

$$d_{2pAO} = d_{H_2MO} - c' \tag{14.45}$$

Substitution of Eqs. (14.24) and (14.44) into Eq. (14.45) gives

$$d_{O2pAO} = 0.64637a_0 = 3.42047\,X\,10^{-11}\ m \tag{14.46}$$

As shown in Eq. (14.18), each $C=O$ bond comprises a factor of 0.75 of the charge-density of double that of the H_2-type ellipsoidal MO. Using the electron configuration of CO_2 (Eq. (14.2)), the radii of the $C1s = 0.17113a_0$ (Eq. (10.51)), $C2s = 0.84317a_0$ (Eq. (10.62)), $O1s = 0.12739a_0$ (Eq. (10.51)), $O2s = 0.59020a_0$ (Eq. (10.62)), and

$O2p = 0.74776a_0$ (Eq. (14.11)) shells and the parameters of the σ MO of CO_2 given by Eqs. (13.3-13.4), (14.23-14.25), and (14.27-14.28), the dimensional diagram and charge-density of the CO_2 MO are shown in Figures 33 and 34, respectively.

SUM OF THE ENERGIES OF THE σ MO AND THE AOs OF THE CARBON DIOXIDE MOLECULE

The energies of the CO_2 σ MO are given by the substitution of the semiprincipal axes (Eqs. (14.23-14.24) and (14.27)) into the energy equations of OH (Eqs. (13.67-13.73)), except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to each σ-MO double bond:

$$V_e = 2^2\left(\frac{3}{4}\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -104.83940\ eV \tag{14.47}$$

$$V_p = 2^2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 49.58464\ eV \tag{14.48}$$

$$T = 2\left(\frac{3}{4}\right)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 14.50438\ eV \tag{14.49}$$

$$V_m = 2^2\left(\frac{3}{4}\right)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -14.50438\ eV \tag{14.50}$$

$$E_T = V_e + T + V_m + V_p \tag{14.51}$$

Substitution of Eqs. (13.60) and (14.47-14.50) into Eq. (14.51) gives

$$E_T(C=O,\sigma) = V_e + T + V_m + V_p = \frac{-4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[\left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}} - 1\right] = -55.25476\ eV \tag{14.52}$$

where $E_T(C=O,\sigma)$ is the total energy of each $C=O$ σ MO of CO_2 given by Eq. (14.19) which is reiteratively matched to Eq. (14.20) within five-significant-figure round off error.

The total energy of CO_2, $E_T(CO_2)$, is given by the sum of $E(ionization;\ C)$ and $E(ionization;\ C^+)$, the sum of the energies of the first and second electrons of carbon (Eqs. (14.12-14.13)) donated to each double bond, the sum of $E(ionization;\ O)$ and two times $E(ionization;\ O^+)$, the energies of the first and second electrons of oxygen (Eqs. (14.14-

14.15)) donated to the double bonds, two times $E_T(O,2p)$, the $O2p$ AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.17)), and two times $E_T(C=O,\sigma)$, the σ MO contribution given by Eq. (14.22):

$$\begin{aligned} E_T(CO_2) &= \begin{pmatrix} E(ionization;\ C)+E(ionization;\ C^+)+E(ionization;\ O) \\ +2E(ionization;\ O^+)+2E_T(O,2p)+2E_T(C=O,\sigma) \end{pmatrix} \\ &= \begin{pmatrix} 11.26030\ eV+24.38332\ eV+13.61806\ eV \\ +2(35.11730\ eV)+2(-32.12759\ eV) \\ -2\left(\frac{4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left(\left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right)\right) \end{pmatrix} \\ &= \begin{pmatrix} 11.26030\ eV+24.38332\ eV+13.61806\ eV \\ +2(35.11730\ eV)+2(-32.12759\ eV)-2(55.25423\ eV) \end{pmatrix} \\ &= -55.26841\ eV \end{aligned} \tag{14.53}$$

VIBRATION OF CO_2

The vibrational energy levels of CO_2 may be solved by determining the Morse potential curve from the energy relationships for the transition from a C atom and two O atoms whose parameters are given by Eqs. (10.115-10.123) and (10.154-10.163), respectively, to a C atom whose parameter r_4 is given by Eq. (10.61), two O atoms whose parameter r_6 is given by Eq. (14.11), and the σ CO_2 MO whose parameters are given by Eqs. (14.23-14.25) and (14.27-14.28). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [4] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF THE CARBON DIOXIDE MOLECULE

The equations of the radiation reaction force of carbon dioxide are the same as those of OH with the substitution of the CO_2 parameters except that there is a factor of four increase in the

central force in Eq. (13.140) due to the double bond. Using Eqs. (13.140-13.142), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{4(0.75)e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 4.16331\ X\ 10^{16}\ rad/s \tag{14.54}$$

where b is given by Eq. (14.27). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 4.16331\ X\ 10^{16}\ rad/s = 27.40365\ eV \tag{14.55}$$

In Eq. (11.181), substitution of $E_T(CO_2)/2$ for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.55) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -27.63421\ eV\sqrt{\frac{2e(27.40365\ eV)}{m_e c^2}} = -0.28619\ eV \tag{14.56}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The transition state comprises $O--CO$, oxygen binding to CO. Vibration of the linear XYZ-molecular transition state corresponds to υ_3 [5] with the maximum kinetic energy localized to the nascent $C-O$ bond. In this case, the kinetic energy of the nuclei is the maximum for this bond. Thus, $\overline{E}_{Kvib}$ is the vibrational energy. The decrease in the energy of the CO_2 MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.56) and $\overline{E}_{Kvib}$, the vibrational energy. Using the experimental CO_2 $E_{vib}(\upsilon_3)$ of 2349 cm^{-1} (0.29124 eV) [6] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(CO_2)$ is

$$\overline{E}_{osc}(CO_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + E_{vib} \tag{14.57}$$

$$\overline{E}_{osc}(CO_2) = -0.28619\ eV + 0.29124\ eV = 0.00505\ eV \tag{14.58}$$

TOTAL AND BOND ENERGIES OF THE CARBON DIOXIDE MOLECULE

$E_{T+osc}(CO_2)$, the total energy of CO_2 including the Doppler term, is given by the sum of $E_T(CO_2)$ (Eq. (14.53)) and $\overline{E}_{osc}(CO_2)$ given by Eq. (14.58):

$$\begin{aligned} E_{T+osc}(CO_2) &= \begin{pmatrix} 2(V_e+T+V_m+V_p)+E(ionization;\ C) \\ +E(ionization;\ C^+)+E(ionization;\ O)+2E(ionization;\ O^+) \\ +2E_T(O,2p)+\overline{E}_{osc}(CO_2) \end{pmatrix} \\ &= \begin{pmatrix} 2E_T(C=O,\sigma)+E(ionization;\ C)+E(ionization;\ C^+) \\ +E(ionization;\ O)+2E(ionization;\ O^+) \\ +2E_T(O,2p)+\overline{E}_{osc}(CO_2) \end{pmatrix} \\ &= E_T(CO_2)+\overline{E}_{osc}(CO_2) \end{aligned} \tag{14.59}$$

$$\begin{aligned} E_{T+osc}(CO_2) = \Bigg\{ & \begin{pmatrix} 2\left(\frac{-4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left(\left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right)\right)+E(ionization;\ C) \\ +E(ionization;\ C^+)+E(ionization;\ O) \\ +2E(ionization;\ O^+)-2\sum_{O,n=4}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) \end{pmatrix} \\ & \begin{pmatrix} \left(1+\frac{1}{2}\sqrt{\frac{2\hbar\sqrt{\frac{4(0.75)e^2}{4\pi\varepsilon_o b^3}}}{m_e}}\right)+E_{vib} \end{pmatrix} \Bigg\} \\ = & -55.26841\ eV-0.28619\ eV+E_{vib} \end{aligned} \tag{14.60}$$

From Eqs. (14.57-14.60), the total energy of the CO_2 MO is

$$\begin{aligned} E_{T+osc}(CO_2) &= -55.25476\ eV+\overline{E}_{osc}(CO_2) \\ &= -55.25476\ eV+0.00505\ eV \\ &= -55.26336\ eV \end{aligned} \tag{14.61}$$

where the experimental E_{vib} was used.

As in the case of the dissociation of the bond of the hydroxyl radical, an oxygen atom is formed with dissociation of CO_2. O has two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is

reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 a_0^3} = \frac{8\pi\mu_o\mu_B^2}{a_0^3} = 0.11441\ eV \tag{14.62}$$

The CO_2 bond dissociation energy, $E_D(CO_2)$, is given by the sum of the energies of the CO and the O atom minus the sum of $E_{T+osc}(CO_2)$ and $E(magnetic)$:

$$E_D(CO_2) = E(CO) + E(O) - \left(E(magnetic) + E_{T+osc}(CO_2)\right) \tag{14.63}$$

The energy of an oxygen atom is given by Eq. (14.14) and $E_T(CO)$ is given by the sum of the experimental energies of C (Eq. (14.12)), O (Eq. (14.14)), and the negative of the bond energy of CO (Eq. (13.914)):

$$E(CO) = -11.26030\ eV - 13.618060\ eV - 11.15696\ eV = -36.03532\ eV \tag{14.64}$$

The energy of O is given by the negative of the corresponding ionization energy given in Eq. (4.14). Thus, the CO_2 bond dissociation energy, $E_D(CO_2)$, given by the Eqs. (4.14) and (14.61-14.64) is

$$\begin{aligned} E_D(CO_2) &= -\left(36.03532\ eV + 13.618060\ eV\right) - \left(E(magnetic) + E_{T+osc}(CO_2)\right) \\ &= -49.65338\ eV - \left(0.11441\ eV - 55.26336\ eV\right) \\ &= 5.49557\ eV \end{aligned} \tag{14.65}$$

The experimental CO_2 bond dissociation energy is [7]

$$E_{D298}(CO_2) = 5.516\ eV \tag{14.66}$$

The results of the determination of bond parameters of CO_2 are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

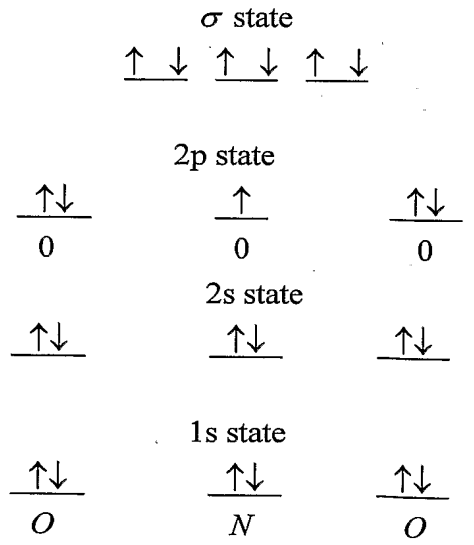
NITROGEN DIOXIDE MOLECULE

The nitrogen dioxide molecule can be formed by the reaction of nitric oxide and an oxygen atom:

$$NO + O \rightarrow NO_2 \tag{14.67}$$

The bonding in the nitrogen dioxide molecule comprises two double bonds, each a H_2-type MO with four paired electrons wherein the central N atom is shared by both bonds such that six electrons can be assigned to the two $N = O$ bonds. Thus, two $N2p$ electrons combine

with the four $O2p$ electrons, two from each O, as a linear combination to form the two overlapping $N=O$ bonds of NO_2. The force balance equation and radius r_7 of the $2p$ shell of N is derived in the Seven-Electron Atoms section. The force balance equation and radius r_8 of the $2p$ shell of O is derived in the Eight-Electron Atoms section. With the formation of each of the two H_2-type MOs by the contribution of two $2p$ electrons each from the N and O atoms, a diamagnetic force arises between the remaining outer shell atomic electrons, the $2s$ and $2p$ electrons of N and O, and the H_2-type MO. This force from N and O causes the H_2-type MO to move to greater principal axes than would result with the Coulombic force alone. But, the factor of two increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining N and O electrons decrease the radii of the corresponding shells such that the energy minimum is achieved that is lower than that of the reactant atoms. The resulting electron configuration of NO_2 is $N1s^2O_1 1s^2O_2 1s^2N2s^2O_1 2s^2O_2 2s^2N2p^1O_1 2p^2O_2 2p^2\sigma^6_{O_2,N,O_1}$ where the subscripts designate the O atom, 1 or 2, σ designates the H_2-type MO, and the orbital arrangement is



(14.68)

Nitrogen dioxide is predicted to be weakly paramagnetic in agreement with observations [1].

FORCE BALANCE OF THE $2p$ SHELL OF THE NITROGEN ATOM OF NITROGEN DIOXIDE

For the N atom, force balance for the outermost $2p$ electron of NO_2 (electron 5) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due to interactions between electron 5 and the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Seven-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of NO (electron 5) due to the nucleus and the inner four electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2}\mathbf{i}_r \tag{14.69}$$

for $r > r_4$. The $2p$ shell possess a +2 external electric field given by Eq. (10.92) for $r > r_5$. The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of N in NO_2 are the same as those of N in NO. They are also the same as those of N in the nitrogen molecule with r_5 replacing r_6 and with an increase of the central field by an integer. The diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contribution is given by Eq. (13.918):

$$\mathbf{F}_{diamagnetic} = -\left(\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{\hbar^2}{12m_e r_5^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{14.70}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved orbital angular momentum of the three orbitals is also the same as that of NO_2 given by Eq. (13.919):

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{3\hbar^2}{m_e r_5^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{14.71}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_5$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is given by Eq. (13.920):

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_5^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{14.72}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.69)) and diamagnetic (Eqs. (14.70) and (14.72)), and paramagnetic (Eq. (14.71)) forces as follows:

$$\frac{m_e v_5^2}{r_5} = \begin{pmatrix} \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12 m_e r_5^2 r_3}\sqrt{s(s+1)} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{s(s+1)} \end{pmatrix} \tag{14.73}$$

Substitution of $v_5 = \frac{\hbar}{m_e r_5}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (14.73) gives:

$$\frac{\hbar^2}{m_e r_5^3} = \frac{(Z-4)e^2}{4\pi\varepsilon_0 r_5^2} - \frac{\hbar^2}{12 m_e r_5^2 r_3}\sqrt{\frac{3}{4}} + \frac{3\hbar^2}{Z m_e r_5^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_5^4 m_e}10\sqrt{\frac{3}{4}} \tag{14.74}$$

The quadratic equation corresponding to Eq. (14.74) is

$$r_5^2 - \frac{\frac{\hbar^2}{m_e}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_5 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right) r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-4)e^2}{4\pi\varepsilon_0} - \left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{14.75}$$

The solution of Eq. (14.75) using the quadratic formula is:

$$r_5 = \frac{\frac{a_0}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-5}{Z-4}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-4)-\left(\frac{1}{12}-\frac{3}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2} \tag{14.76}$$

r_3 *in units of* a_0

The positive root of Eq. (14.76) must be taken in order that $r_5 > 0$. Substitution of $\frac{r_3}{a_0} = 0.69385$ (Eq. (10.62) with $Z = 7$) into Eq. (14.76) gives

$$r_5 = 0.74841 a_0 \tag{14.77}$$

FORCE BALANCE OF THE $2p$ SHELL OF EACH OXYGEN ATOM OF NITROGEN DIOXIDE

For each O atom, force balance for the outermost $2p$ electron of NO_2 (electron 6) is achieved between the centrifugal force and the Coulombic and magnetic forces that arise due

to interactions between electron 6 and the other $2p$ electron as well as the $2s$-shell electrons due to spin and orbital angular momentum. The forces used are derived in the Eight-Electron Atoms section. The central Coulomb force on the outer-most $2p$ shell electron of NO_2 (electron 6) due to the nucleus and the inner five electrons is given by Eq. (10.70) with the appropriate charge and radius:

$$\mathbf{F}_{ele} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2}\mathbf{i}_r \tag{14.78}$$

for $r > r_5$. The $2p$ shell possess an external electric field of +2 given by Eq. (10.92) for $r > r_6$. The energy is minimized with conservation of angular momentum. This condition is met when the magnetic forces of O in NO_2 are the same as those of O in NO. The diamagnetic force, $\mathbf{F}_{diamagnetic}$, of Eq. (10.82) due to the p-orbital contribution given by Eq. (13.927) is

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}\right)\frac{\hbar^2}{4m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r = -\frac{2\hbar^2}{12m_e r_6^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r \tag{14.79}$$

And, $\mathbf{F}_{mag\ 2}$ corresponding to the conserved spin and orbital angular momentum given by Eq. (13.928) is

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{2\hbar^2}{m_e r_6^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r \tag{14.80}$$

The electric field external to the $2p$ shell given by Eq. (10.92) for $r > r_6$ gives rise to a second diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, given by Eq. (10.93). $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius given by Eq. (13.929) is

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_6^4}10\sqrt{s(s+1)}\mathbf{i}_r \tag{14.81}$$

In addition, the contribution of two $2p$ electrons in the formation of the σ MO gives rise to a paramagnetic force on the remaining paired $2p$ electrons. The force $\mathbf{F}_{mag\ 3}$ is given by Eq. (13.930) is

$$\mathbf{F}_{mag\ 3} = \frac{\hbar^2}{4m_e r_6^3}\sqrt{s(s+1)}\mathbf{i}_r \tag{14.82}$$

The radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric (Eq. (14.78)) and diamagnetic (Eqs. (14.79) and (14.81)), and

paramagnetic (Eqs. (14.80) and (14.82)) forces as follows:

$$\frac{m_e v_6^2}{r_6} = \left(\begin{array}{l} \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12 m_e r_6^2 r_3}\sqrt{s(s+1)} + \frac{2\hbar^2}{Z m_e r_6^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{s(s+1)} + \frac{\hbar^2}{4 m_e r_6^3}\sqrt{s(s+1)} \end{array} \right) \tag{14.83}$$

Substitution of $v_6 = \frac{\hbar}{m_e r_6}$ (Eq. (1.56)) and $s = \frac{1}{2}$ into Eq. (14.83) gives:

$$\frac{\hbar^2}{m_e r_6^3} - \frac{\hbar^2}{4 m_e r_6^3}\sqrt{\frac{3}{4}} = \frac{(Z-5)e^2}{4\pi\varepsilon_0 r_6^2} - \frac{2\hbar^2}{12 m_e r_6^2 r_3}\sqrt{\frac{3}{4}} + \frac{2\hbar^2}{Z m_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_6^4 m_e}10\sqrt{\frac{3}{4}} \tag{14.84}$$

The quadratic equation corresponding to Eq. (14.84) is

$$r_6^2 - \frac{\frac{\hbar^2}{m_e}\left(1-\frac{\sqrt{3}}{8}\right)}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} r_6 - \frac{\frac{\hbar^2}{m_e}\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3 10\sqrt{\frac{3}{4}}}{\left(\frac{(Z-5)e^2}{4\pi\varepsilon_0} - \left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\hbar^2}{m_e r_3}\sqrt{\frac{3}{4}}\right)} = 0 \tag{14.85}$$

The solution of Eq. (14.85) using the quadratic formula is:

$$r_6 = \frac{\frac{a_0\left(1-\frac{\sqrt{3}}{8}\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1-\frac{\sqrt{3}}{8}}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-6}{Z-5}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-5)-\left(\frac{2}{12}-\frac{2}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2} \tag{14.86}$$

r_3 *in units of* a_0

The positive root of Eq. (14.86) must be taken in order that $r_6 > 0$. Substitution of $\frac{r_3}{a_0} = 0.59020$ (Eq. (10.62) with $Z = 8$) into Eq. (14.86) gives

$$r_6 = 0.70460 a_0 \tag{14.87}$$

ENERGIES OF THE $2p$ SHELLS OF THE NITROGEN ATOM AND

OXYGEN ATOMS OF NITROGEN DIOXIDE

Consider the determination of the total energy of NO_2 from the reaction of a nitrogen atom with two oxygen atoms. With the formation of each H_2-type MO by the contribution of two $2p$ electrons from each of the N and the two O atoms, the total energy of the NO_2 molecule, which is subtracted from the sum of the energies of the nitrogen and oxygen atoms to determine the bond energy, is increased by the ionization energies of N, N^+, O, and $2O^+$ given by Eqs. (14.88-14.91), respectively. Experimentally, the energies are [2]

$$E(ionization;\ N) = 14.53414\ eV \tag{14.88}$$

$$E(ionization;\ N^+) = 29.6013\ eV \tag{14.89}$$

$$E(ionization;\ O) = 13.61806\ eV \tag{14.90}$$

$$E(ionization;\ O^+) = 35.11730\ eV \tag{14.91}$$

In addition, the central forces on the $2p$ shells of the N and O atoms are increased with the formation of the σ MOs which reduces each shell's radius and increases its total energy. The change per bond is the same as that of NO since the final radii given by Eq. (14.77) and (14.87) are the same for NO and NO_2. The Coulombic energy terms of the total energy of the N and O atoms at the new radii are calculated and added to the ionization energies of N, N^+, O, and $2O^+$, and the energy of the σ MOs to give the total energy of NO_2. Then, the bond energy is determined from the total NO_2 energy.

The radius r_7 of the nitrogen atom before bonding is given by Eq. (10.142):

$$r_7 = 0.93084 a_0 \tag{14.92}$$

Using the initial radius r_7 of the N atom and the final radius r_5 of the $N2p$ shell (Eq. (14.77)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(N,2p)$ of the Coulombic energy change of the $N2p$ electrons of the N atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(N,2p) &= -\sum_{n=4}^{4} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_7}\right) \\ &= -(13.60580\ eV)(0.26186)(3) \\ &= -10.68853\ eV \end{aligned} \tag{14.93}$$

The radius r_8 of the oxygen atom before bonding is given by Eq. (10.162):

$$r_8 = a_0 \tag{14.94}$$

Using the initial radius r_8 of the O atom and the final radius r_6 of the $O2p$ shell (Eq. (14.87)) and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell, the sum $E_T(O,2p)$ of the Coulombic energy change of the $O2p$ electrons of the O atom is determined using Eq. (10.102):

$$\begin{aligned} E_T(O,2p) &= \sum_{n=4}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) \\ &= (13.60580\ eV)\left(0.41925a_0^{-1}\right)(3+4) \\ &= -39.92918\ eV \end{aligned} \tag{14.95}$$

FORCE BALANCE OF THE σ MO OF NITROGEN DIOXIDE

The force balance can be considered due to a second pair of two electrons binding to a molecular ion having $+2e$ at each focus and a first bound pair. Then, the forces are the same as those of a molecule ion having $+e$ at each focus. The diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for each σ-MO of the NO_2 molecule due to the two paired electrons in the $O2p$ shell is given by Eq. (13.633) with $n_e = 2$:

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{14.96}$$

This is also the corresponding force of NO given by Eq. (13.942). $\mathbf{F}_{diamagneticMO2}$ of the nitrogen dioxide molecule comprising nitrogen with charge $Z_1 = 7$ and $|L_1| = \hbar$ and $|L_2| = \sqrt{\frac{3}{4}}\hbar$ and the two oxygen atoms, each with $Z_2 = 8$ and $|L_3| = \hbar$ is given by the corresponding sum of the contributions. Using Eq. (13.835), $\mathbf{F}_{diamagneticMO2}$ for NO_2 is

$$\mathbf{F}_{diamagneticMO2} = \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi \tag{14.97}$$

This is also the corresponding force of NO given by Eq. (13.943) except the term due to oxygen is twice that of NO due to the two oxygen atoms of NO_2. The general force balance equation for the σ-MO of the nitrogen dioxide molecule given by Eqs. (11.200), and (14.97-14.98) is also the same as that of CN (Eq. (14.836)) except for the doubling of the $\frac{2}{Z_2}$ term due to the two oxygen atoms:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{14.98}$$

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D - \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D \tag{14.99}$$

$$\left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D \tag{14.100}$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2}\right) a_0 \tag{14.101}$$

Substitution of $Z_1 = 7$ and $Z_2 = 8$ into Eq. (14.101) gives

$$a = 2.51658 a_0 = 1.33171\ X\ 10^{-10}\ m \tag{14.102}$$

Substitution of Eq. (14.102) into Eq. (11.79) is

$$c' = 1.12173 a_0 = 5.93596\ X\ 10^{-11}\ m \tag{14.103}$$

The internuclear distance given by multiplying Eq. (14.103) by two is

$$2c' = 2.24347 a_0 = 1.18719\ X\ 10^{-10}\ m \tag{14.104}$$

The experimental bond distance is [3]

$$2c' = 1.193\ X\ 10^{-10}\ m \tag{14.105}$$

Substitution of Eqs. (14.102-14.103) into Eq. (11.80) is

$$b = c = 2.25275 a_0 = 1.19210\ X\ 10^{-10}\ m \tag{14.106}$$

Substitution of Eqs. (14.102-14.103) into Eq. (11.67) is

$$e = 0.44574 \tag{14.107}$$

The bonding in the nitrogen dioxide molecule comprises two double bonds, each a H_2-type MO with four paired electrons wherein the central N atom is shared by both bonds such that six electrons can be assigned to the two $N=O$ bonds. Thus, two $N2p$ electrons combine with the four $O2p$ electrons, two from each O, as a linear combination to form the two overlapping $N=O$ bonds of NO_2. Using the electron configuration of NO_2 (Eq.

(14.68)), the radii of the $N1s = 0.14605a_0$ (Eq. (10.51)), $N2s = 0.69385a_0$ (Eq. (10.62)), $N2p = 0.74841a_0$ (Eq. (14.77)), $O1s = 0.12739a_0$ (Eq. (10.51)), $O2s = 0.59020a_0$ (Eq. (10.62)), and $O2p = 0.70460a_0$ (Eq. (14.87)) shells and the parameters of the σ MOs of NO_2 given by Eqs. (13.3-13.4), (14.102-14.104), and (14.106-14.107), the dimensional diagram and charge-density of the NO_2 MO are shown in Figures 35 and 36, respectively.

SUM OF THE ENERGIES OF THE σ MOs AND THE AOs OF NITROGEN DIOXIDE

The energies of each NO_2 σ MO are the same as those of NO (Eqs. (13.954-13.958)). They are given by the substitution of the semiprincipal axes (Eqs. (14.102-14.103) and (14.106)) into the energy equations (Eqs. (11.207-11.212)) of H_2 except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the σ-MO double bond with two pairs of paired electrons:

$$V_e = 2^2 \frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -93.03032\ eV \tag{14.108}$$

$$V_p = 2^2 \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 48.51704\ eV \tag{14.109}$$

$$T = 2\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 9.24176\ eV \tag{14.110}$$

$$V_m = 2^2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -9.24176\ eV \tag{14.111}$$

$$E_T = V_e + T + V_m + V_p \tag{14.112}$$

Substitution of Eqs. (11.79) and (14.108-14.111) into Eq. (14.112) gives

$$E_T(N=O,\sigma) = \frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 4 \right) = -44.51329\ eV \tag{14.113}$$

where $E_T(N=O,\sigma)$ is the total energy of each σ MO of NO_2. The total energy of NO_2, $E_T(NO_2)$, is given by the sum of $E(ionization; N)$ and $E(ionization; N^+)$, the sum of the energies of the first and second electrons of nitrogen (Eqs. (14.88-14.89)) donated to each

double bond, the sum of $E(ionization;\ O)$ and two times $E(ionization;\ O^+)$, the energies of the first and second electrons of oxygen (Eqs. (14.90-14.91)) donated to the double bonds, $E_T(N,2p)$, the $N2p$ AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.93)), two times $E_T(O,2p)$, the $O2p$ AO contribution due to the decrease in radius with the formation of each bond (Eq. (14.95)), and two times $E_T(N=O,\sigma)$, the σ MO contribution given by Eq. (14.113):

$$\begin{aligned}
E_T(NO_2) &= \begin{pmatrix} E(ionization;\ N)+E(ionization;\ N^+) \\ +E(ionization;\ O)+2E(ionization;\ O^+)+E_T(N,2p) \\ +2E_T(O,2p)+2E_T(N=O,\sigma) \end{pmatrix} \\
&= \begin{pmatrix} 14.53414\ eV+29.6013\ eV+13.61806\ eV \\ +2(35.11730\ eV)+(-10.68853)+2(-39.92918\ eV) \\ +2\left(\dfrac{-e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2}}}\left(8\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2}}}{a-\sqrt{\dfrac{aa_0}{2}}}-4\right)\right) \end{pmatrix} \\
&= \begin{pmatrix} 14.53414\ eV+29.6013\ eV+13.61806\ eV \\ +2(35.11730\ eV)+(-10.68853) \\ +2(-39.92918\ eV)+2(-44.51329\ eV) \end{pmatrix} \\
&= -51.58536\ eV
\end{aligned} \tag{14.114}$$

VIBRATION OF NO_2

The vibrational energy levels of NO_2 may be solved by determining the Morse potential curve from the energy relationships for the transition from a N atom and two O atoms whose parameters are given by Eqs. (10.134-10.143) and (10.154-10.163), respectively, to a N atom whose parameter r_5 is given by Eq. (14.77), two O atoms whose parameter r_6 is given by Eq. (14.87), and the σ MOs whose parameters are given by Eqs. (14.102-14.104) and (14.106.-14.107). As shown in the Vibration of Hydrogen-type Molecular Ions section, the harmonic oscillator potential energy function can be expanded about the internuclear distance and expressed as a Maclaurin series corresponding to a Morse potential after Karplus and Porter (K&P) [4] and after Eq. (11.134). Treating the Maclaurin series terms as anharmonic perturbation terms of the harmonic states, the energy corrections can be found by perturbation methods.

THE DOPPLER ENERGY TERMS OF NITROGEN DIOXIDE

The equations of the radiation reaction force of nitrogen dioxide are the same as those of NO with the substitution of the NO_2 parameters. Using Eq. (13.961), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{4e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 2.07110\,X\,10^{16}\ rad/s \tag{14.115}$$

where a is given by Eq. (14.102). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.07110\,X\,10^{16}\ rad/s = 13.63231\ eV \tag{14.116}$$

In Eq. (11.181), substitution of $E_T(NO_2)/2$ for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.116) for $\overline{E}_K$ gives the Doppler energy of the electrons of the reentrant orbit:

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -25.79268\ eV\sqrt{\frac{2e(13.63231\ eV)}{m_e c^2}} = -0.18840\ eV \tag{14.117}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The transition state comprises $O--NO$, oxygen binding to NO. As in the case of CO_2 bond formation, vibration in the transition state corresponds to υ_3 [5] with the maximum kinetic energy localized to the nascent $N-O$ bond. In this case, the kinetic energy of the nuclei is the maximum for this bond. Thus, $\overline{E}_{Kvib}$ is the vibrational energy. The decrease in the energy of the NO_2 MO due to the reentrant orbit in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.117) and $\overline{E}_{Kvib}$, the vibrational energy. Using the experimental NO_2 $E_{vib}(\upsilon_3)$ of 1618 cm^{-1} $(0.20061\ eV)$ [6] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(NO_2)$ is

$$\overline{E}_{osc}(NO_2) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + E_{vib} \tag{14.118}$$

$$\overline{E}_{osc}(NO_2) = -0.18840\ eV + 0.20061\ eV = 0.01221\ eV \tag{14.119}$$

TOTAL AND BOND ENERGIES OF NITROGEN DIOXIDE

$E_{T+osc}(NO_2)$, the total energy of NO_2 including the Doppler term, is given by the sum of $E_T(NO_2)$ (Eq. (14.114)) and $\overline{E}_{osc}(NO_2)$ given by Eq. (14.119):

$$\begin{aligned} E_{T+osc}(NO_2) &= \begin{pmatrix} 2(V_e+T+V_m+V_p)+E(ionization;\ N)+E(ionization;\ N^+) \\ +E(ionization;\ O)+2E(ionization;\ O^+) \\ +E_T(N,2p)+2E_T(O,2p)+\overline{E}_{osc}(NO_2) \end{pmatrix} \\ &= \begin{pmatrix} 2E_T(N=O,\sigma)+E(ionization;\ N)+E(ionization;\ N^+) \\ +E(ionization;\ O)+2E(ionization;\ O^+) \\ +E_T(N,2p)+2E_T(O,2p)+\overline{E}_{osc}(NO_2) \end{pmatrix} \\ &= E_T(NO_2)+\overline{E}_{osc}(NO_2) \end{aligned} \tag{14.120}$$

$$\begin{aligned} E_{T+osc}(NO_2) = \Bigg\{ & \Bigg(2\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-4 \right) \right) \\ & E(ionization;\ N)+E(ionization;\ N^+) \\ & +E(ionization;\ O)+2E(ionization;\ O^+) \\ & -\sum_{N,n=4}^{4}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_5}-\frac{1}{r_7}\right)-2\sum_{O,n=4}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_6}-\frac{1}{r_8}\right) \Bigg) \\ & \left(1+\frac{1}{2}\sqrt{\frac{2\hbar\sqrt{\frac{4e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}} \right)+E_{vib} \Bigg\} \\ = & -51.58536\ eV-0.18840\ eV+E_{vib} \end{aligned} \tag{14.121}$$

From Eqs. (14.119-14.121), the total energy of the NO_2 MO is

$$\begin{aligned} E_{T+osc}(NO_2) &= -51.58536\ eV+\overline{E}_{osc}(NO_2) \\ &= -51.58536\ eV+0.01221\ eV \\ &= -51.57315\ eV \end{aligned} \tag{14.122}$$

where the experimental E_{vib} was used.

As in the case of the dissociation of the bond of the hydroxyl radical, an oxygen atom is formed with dissociation of NO_2. O has two unpaired electrons as shown in Eq. (13.55) which interact to stabilize the atom as shown by Eq. (10.161-10.162). The lowering of the energy of the reactants decreases the bond energy. Thus, the total energy of oxygen is

reduced by the energy in the field of the two magnetic dipoles given by Eq. (7.46) and Eq. (13.101):

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 a_0^3}=\frac{8\pi\mu_o\mu_B^2}{a_0^3}=0.11441\ eV \tag{14.123}$$

The NO_2 bond dissociation energy, $E_D(NO_2)$, is given by the sum of the energies of the NO and the O atom minus the sum of $E_{T+osc}(NO_2)$ and $E(magnetic)$:

$$E_D(NO_2)=E(NO)+E(O)-\left(E(magnetic)+E_{T+osc}(NO_2)\right) \tag{14.124}$$

The energy of an oxygen atom is given by the negative of Eq. (14.90), and $E_T(NO)$ is given by the sum of the experimental energies of N (negative of Eq. (14.88)), O, and the negative of the bond energy of NO (Eq. (13.974)):

$$E(NO)=-14.53414\ eV-13.618060\ eV-6.53529\ eV=-34.68749\ eV \tag{14.125}$$

Thus, the NO_2 bond dissociation energy, $E_D(NO_2)$, given by Eqs. (4.90) and (14.112-14.125) is

$$\begin{aligned}E_D(NO_2)&=-(34.68749\ eV+13.618060\ eV)-\left(E(magnetic)+E_{T+osc}(NO_2)\right)\\&=-48.30555\ eV-(0.11441\ eV-51.57315\ eV)\\&=3.15319\ eV\end{aligned} \tag{14.126}$$

The experimental NO_2 bond dissociation energy is [7]

$$E_{D298}(NO_2)=3.161\ eV \tag{14.127}$$

BOND ANGLE OF NO_2

The NO_2 MO comprises a linear combination of two $N=O$-bond MOs. A bond is also possible between the two O atoms of the $N=O$ bonds. Such $O=O$ bonding would decrease the $N=O$ bond strength since electron density would be shifted from the $N=O$ bonds to the $O=O$ bond. Thus, the bond angle between the two $N=O$ bonds is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal O atoms of the $N=O$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $O=O$ ellipsoidal MO is

$$c'=a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}}=\sqrt{\frac{aa_0}{2}} \tag{14.128}$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.129}$$

The length of the semiminor axis of the prolate spheroidal $O=O$ MO $b=c$ is given by Eq. (13.167).

The component energies and the total energy E_T of the $O=O$ bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of H_2 except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to the $O=O$ double bond with two pairs of paired electrons. Substitution of Eq. (14.128) into Eqs. (11.207-11.212) gives

$$0 = \left[\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}} \left(8\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}} - 4 \right) \left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{4e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}} \right] \right. \\ \left. + \frac{1}{2}\hbar\sqrt{\frac{\frac{4e^2}{8\pi\varepsilon_o a^3} - \frac{4e^2}{8\pi\varepsilon_o (a+c')^3}}{8m_p}} \right] \tag{14.130}$$

From the energy relationship given by Eq. (14.130) and the relationship between the axes given by Eqs. (14.128-14.129) and (13.167-14.168), the dimensions of the $O=O$ MO can be solved.

The most convenient way to solve Eq. (14.130) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 8.3360a_0 = 4.4112\,X\,10^{-10}\ m \tag{14.131}$$

Substitution of Eq. (14.131) into Eq. (14.128) gives

$$c' = 2.0416a_0 = 1.0804\,X\,10^{-10}\ m \tag{14.132}$$

The internuclear distance given by multiplying Eq. (14.132) by two is

$$2c' = 4.0831a_0 = 2.1607\,X\,10^{-10}\ m \tag{14.133}$$

Substitution of Eqs. (14.131-14.132) into Eq. (14.167) gives

$$b = c = 8.0821a_0 = 4.2769\,X\,10^{-10}\ m \tag{14.134}$$

Substitution of Eqs. (14.131-14.132) into Eq. (14.168) gives

$$e = 0.2449 \tag{14.135}$$

From, $2c'_{C=C}$ (Eq. (14.133)), the distance between the two O atoms when the total energy of the corresponding MO is zero (Eq. (14.130)), and $2c'_{N=O}$ (Eq. (14.104)), the

internuclear distance of each $N=O$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eqs. (13.240-13.242), the bond angle θ between the $N=O$ bonds is

$$\begin{aligned}\theta &= \cos^{-1}\left(\frac{2(2.24347)^2-(4.0831)^2}{2(2.24347)^2}\right)\\ &= \cos^{-1}(-0.6562)\\ &= 131.012^\circ\end{aligned} \tag{14.136}$$

The experimental angle between the $N=O$ bonds is [3]

$$\theta = 134.1^\circ \tag{14.137}$$

The results of the determination of bond parameters of NO_2 are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

ETHANE MOLECULE (CH_3CH_3)

The ethane molecule CH_3CH_3 is formed by the reaction of two methyl radicals:

$$CH_3 + CH_3 \rightarrow CH_3CH_3 \tag{14.138}$$

CH_3CH_3 can be solved using the same principles as those used to solve CH_3, wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of three H atomic orbitals (AOs) combine with two sets of three carbon $2sp^3$ HOs to form two methyl groups comprising a linear combination of six diatomic H_2-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two CH_3 groups bond by forming a H_2-type MO between the remaining $C2sp^3$ HO on each carbon.

FORCE BALANCE OF THE $C-C$-BOND MO OF ETHANE

CH_3CH_3 comprises a chemical bond between two CH_3 radicals wherein each methyl radical comprises three chemical bonds between carbon and hydrogen atoms. The solution of the parameters of CH_3 is given in the Methyl Radical (CH_3) section. Each $C-H$ bond of

CH_3 having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% H_2-type ellipsoidal MO and 25% $C2sp^3$ HO. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H_2, each of the three $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the CH_3 MO that has the symmetry of an s orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

Two CH_3 radicals bond to form CH_3CH_3 by forming a MO between the two remaining $C2sp^3$-HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between two $C2sp^3$ HOs to form a molecular orbital (MO) comprising two spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy.

As in the case of the $C-H$ bonds, the $C-C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each C atom. The energy of the H_2-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of OH, NH, CH, and the $C=O$-bond MO of CO_2, the $C-C$-bond MO of ethane must comprise 75% of a H_2-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C-C$-bond MO must comprise two $C2sp^3$HOs and 75% of a H_2-type ellipsoidal MO divided between the two $C2sp^3$ HOs:

$$2\,C2sp^3 + 0.75\,H_2\ MO \rightarrow C-C-bond\ MO \tag{14.139}$$

The linear combination of the H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C-C$-bond MO to achieve an energy minimum. The force balance of the $C-C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.139) and the energy matching condition between the $C2sp^3$-HO components of the MO.

Similarly, the energies of each CH_3 MO involve each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the H_2-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. This energy is determined by the considering the effect of the donation of 25% electron density from the two $C2sp^3$ HOs to the $C-C$-bond MO. The $2sp^3$ hybridized orbital arrangement given by Eq. (13.422) is

$$\begin{array}{cccc} & & 2sp^3 \text{ state} & \\ \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} & \underline{\uparrow} \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \tag{14.140}$$

where the quantum numbers (ℓ, m_ℓ) are below each electron. The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C,2sp^3\right)$ of calculated energies of C, C^+, C^{2+}, and C^{3+} from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned} E_T\left(C,2sp^3\right) &= 64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 11.27671\ eV \\ &= 148.25751\ eV \end{aligned} \tag{14.141}$$

which agrees well with the sum of 148.02532 eV from the experimental [2] values. Consider the case of the $C2sp^3$ HO of each methyl radical. The orbital-angular-momentum interactions cancel such that the energy of the $E_T\left(C,2sp^3\right)$ is purely Coulombic. By considering that the central field decreases by an integer for each successive electron of the shell, the radius r_{2sp^3} of the $C2sp^3$ shell may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{2sp^3} = \sum_{n=2}^{5} \frac{(Z-n)e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)} = \frac{10e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)} = 0.91771a_0 \tag{14.142}$$

where $Z=6$ for carbon. Using Eqs. (10.102) and (14.142), the Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E_{Coulomb}\left(C,2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.91771a_0}=-14.82575\ eV \tag{14.143}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152) at the initial radius of the $2s$ electrons. From Eq. (10.62) with $Z=6$, the radius r_3 of $C2s$ shell is

$$r_3=0.84317a_0 \tag{14.144}$$

Using Eqs. (13.152) and (14.144), the unpairing energy is

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}=\frac{8\pi\mu_o\mu_B^2}{\left(0.84317a_0\right)^3}=0.19086\ eV \tag{14.145}$$

Using Eqs. (14.143) and (14.145), the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$\begin{aligned}E\left(C,2sp^3\right)&=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}\\&=-14.82575\ eV+0.19086\ eV\\&=-14.63489\ eV\end{aligned} \tag{14.146}$$

Next, consider the formation of the $C-C$-bond MO of ethane from two methyl radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C_{ethane},2sp^3\right)$ of calculated energies of $C2sp^3$, C^+, C^{2+}, and C^{3+} from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned}E_T\left(C_{ethane},2sp^3\right)&=-\left(64.3921\ eV+48.3125\ eV+24.2762\ eV+E\left(C,2sp^3\right)\right)\\&=-\left(64.3921\ eV+48.3125\ eV+24.2762\ eV+14.63489\ eV\right)\\&=-151.61569\ eV\end{aligned} \tag{14.147}$$

where $E\left(C,2sp^3\right)$ is the sum of the energy of C, $-11.27671\ eV$, and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the $E_T\left(C_{ethane},2sp^3\right)$ is purely Coulombic.

The sharing of electrons between two $C2sp^3$ HOs to form a $C-C$-bond MO permits

each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $C2sp^3$ HO donates an excess of 25% of its electron density to the $C-C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethane2sp^3}$ of the $C2sp^3$ shell of ethane may be calculated from the Coulombic energy using Eq. (10.102):

$$\begin{aligned} r_{ethane2sp^3} &= \left(\sum_{n=2}^{5}(Z-n)-0.25\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} \\ &= \frac{9.75e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} \\ &= 0.87495a_0 \end{aligned} \tag{14.148}$$

Using Eqs. (10.102) and (14.148), the Coulombic energy $E_{Coulomb}\left(C_{ethane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$\begin{aligned} E_{Coulomb}\left(C_{ethane},2sp^3\right) &= \frac{-e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}} \\ &= \frac{-e^2}{8\pi\varepsilon_0 0.87495a_0} \\ &= -15.55033\ eV \end{aligned} \tag{14.149}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.149), the energy $E\left(C_{ethane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$\begin{aligned} E\left(C_{ethane},2sp^3\right) &= \frac{-e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} \\ &= -15.55033\ eV + 0.19086\ eV \\ &= -15.35946\ eV \end{aligned} \tag{14.150}$$

Thus, $E_T\left(C-C,2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C-C$-bond MO is given by the difference between Eq. (14.146) and Eq. (14.150):

$$\begin{aligned} E_T\left(C-C,2sp^3\right) &= E\left(C_{ethane},2sp^3\right)-E\left(C,2sp^3\right) \\ &= -15.35946\ eV-\left(-14.63489\ eV\right) \\ &= -0.72457\ eV \end{aligned} \tag{14.151}$$

The H_2-type ellipsoidal MO comprises 75% of the $C-C$-bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to the $C-C$-bond MO causes the electron charge density in Eq. (11.65) to be is given by $\frac{-e}{2}=-0.5e$. Thus, the force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci given by Eq. (11.65) is

$$k'=\frac{(0.5)2e^2}{4\pi\varepsilon_0} \tag{14.152}$$

The distance from the origin to each focus c' is given by substitution of Eq. (14.152) into Eq. (13.60). Thus, the distance from the origin of the $C-C$-bond MO to each focus c' is given by

$$c'=a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 a}}=\sqrt{aa_0} \tag{14.153}$$

The internuclear distance from Eq. (14.153) is

$$2c'=2\sqrt{aa_0} \tag{14.154}$$

The length of the semiminor axis of the prolate spheroidal $C-C$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C-C$-bond MO. Since the $C-C$-bond MO comprises a H_2-type-ellipsoidal MO that transitions to the $C_{ethane}2sp^3$ HO of each carbon, the energy $E\left(C_{ethane},2sp^3\right)$ in Eq. (14.150) adds to that of the H_2-type ellipsoidal MO to give the total energy of the $C-C$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C-C$-bond MO are solved. Similarly, $E\left(C_{ethane},2sp^3\right)$ is added to the energy of the H_2-type ellipsoidal MO of each $C-H$ bond of the methyl groups to give its total energy. From the energy equation and the relationship between the axes, the dimensions of the equivalent $C-H$-bond MOs of the methyl groups in ethane are solved.

The general equations for the energy components of V_e, V_p, T, V_m, and E_T of the $C-C$-bond MO are the same as those of the CH MO as well as each $C-H$-bond MO of the methyl groups except that energy of the $C_{ethane}2sp^3$ HO is used. Since the prolate

spheroidal H_2-type MO transitions to the $C_{ethane}2sp^3$ HO of each carbon and the energy of the $C_{ethane}2sp^3$ shell must remain constant and equal to the $E\left(C_{ethane},2sp^3\right)$ given by Eq. (14.150), the total energy $E_T\left(C-C,\sigma\right)$ of the σ component of the $C-C$-bond MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{ethane}2sp^3$ HO and the H_2-type ellipsoidal MO that forms the σ component of the $C-C$-bond MO as given by Eq. (14.139) with the electron charge redistribution. Using Eqs. (13.431) and (14.150), $E_T\left(C-C,\sigma\right)$ is given by

$$\begin{aligned} E_T\left(C-C,\sigma\right) &= E_T + E\left(C_{ethane},2sp^3\right) \\ &= -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV \end{aligned} \tag{14.155}$$

To match the boundary condition that the total energy of the entire the H_2-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_T\left(C-C,\sigma\right)$ given by Eq. (14.155) is set equal to Eq. (13.75):

$$\begin{aligned} E_T\left(C-C,\sigma\right) &= -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV \\ &= -31.63536831\ eV \end{aligned} \tag{14.156}$$

From the energy relationship given by Eq. (14.156) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the $C-C$-bond MO can be solved.

Substitution of Eq. (14.153) into Eq. (14.156) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right]=e16.27589 \tag{14.157}$$

The most convenient way to solve Eq. (14.157) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 2.10725a_0 = 1.11511\ X\ 10^{-10}\ m \tag{14.158}$$

Substitution of Eq. (14.158) into Eq. (14.153) gives

$$c' = 1.45164a_0 = 7.68173\ X\ 10^{-11}\ m \tag{14.159}$$

The internuclear distance given by multiplying Eq. (14.159) by two is

$$2c' = 2.90327a_0 = 1.53635\ X\ 10^{-10}\ m \tag{14.160}$$

The experimental bond distance is [3]

$$2c' = 1.5351\,X\,10^{-10}\ m \tag{14.161}$$

Substitution of Eqs. (14.158-14.159) into Eq. (13.62) gives

$$b = c = 1.52750a_0 = 8.08317\,X\,10^{-11}\ m \tag{14.162}$$

Substitution of Eqs. (14.158-14.159) into Eq. (13.63) gives

$$e = 0.68888 \tag{14.163}$$

The nucleus of the C atoms comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{ethane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{ethane2sp^3} = 0.87495a_0$ is the radius of the $C_{ethane}2sp^3$ shell. Substitution of Eqs. (14.158-14.159) into Eq. (13.261) gives

$$\theta' = 67.33° \tag{14.164}$$

Then, the angle $\theta_{C-C_{ethane}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-C_{ethane}2sp^3HO} = 180° - 67.33° = 112.67° \tag{14.165}$$

as shown in Figure 37.

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C-C_{ethane},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C_{ethane}2sp^3$ radial vector obeys the following relationship:

$$r_{ethane2sp^3}\sin\theta_{C-C_{ethane}2sp^3HO} = 0.87495a_0\sin\theta_{C-C_{ethane}2sp^3HO} = b\sin\theta_{C-C_{ethane},H_2MO} \tag{14.166}$$

such that

$$\theta_{C-C_{ethane},H_2MO} = \sin^{-1}\frac{0.87495a_0\sin\theta_{C-C_{ethane}2sp^3HO}}{b} = \sin^{-1}\frac{0.87495a_0\sin 112.67°}{b} \tag{14.167}$$

with the use of Eq. (14.166). Substitution of Eq. (14.162) into Eq. (14.167) gives

$$\theta_{C-C_{ethane},H_2MO} = 31.91° \tag{14.168}$$

Then, the distance d_{C-C_{ethane},H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-C_{ethane},H_2MO} = a\cos\theta_{C-C_{ethane},H_2MO} \tag{14.169}$$

Substitution of Eqs. (14.158) and (14.168) into Eq. (14.169) gives

$$d_{C-C_{ethane},H_2MO} = 1.78885a_0 = 9.46617\,X\,10^{-11}\ m \tag{14.170}$$

The distance $d_{C-C_{ethane}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-C_{ethane}2sp^3HO} = d_{C-C_{ethane},H_2MO} - c' \tag{14.171}$$

Substitution of Eqs. (14.159) and (14.170) into Eq. (14.171) gives

$$d_{C-C_{ethane}2sp^3HO} = 0.33721a_0 = 1.78444\,X\,10^{-11}\ m \tag{14.172}$$

FORCE BALANCE OF THE CH_3 MOs OF ETHANE

Each of the two equivalent CH_3 MOs must comprise three $C-H$ bonds with each comprising 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.540):

$$3\left[1\,C2sp^3 + 0.75\,H_2\ MO\right] \rightarrow CH_3\ MO \tag{14.173}$$

The force balance of the CH_3 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.540) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH_3 MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the three prolate spheroidal $C-H$-bond MOs comprises an H_2-type-ellipsoidal MO that transitions to the $C_{ethane}2sp^3$ HO of ethane, the energy $E\left(C_{ethane},2sp^3\right)$ of Eq. (14.150) adds to that of the three corresponding H_2-type ellipsoidal MOs to give the total energy of the CH_3 MO. From the energy equation and the relationship between the axes, the dimensions of the CH_3 MO are solved.

The energy components of V_e, V_p, T, and V_m are the same as those of methyl radical, three times those of CH corresponding to the three $C-H$ bonds except that energy of the $C_{ethane}2sp^3$ HO is used. Since the each prolate spheroidal H_2-type MO transitions to the $C_{ethane}2sp^3$ HO and the energy of the $C_{ethane}2sp^3$ shell must remain constant and equal to the $E\left(C_{ethane},2sp^3\right)$ given by Eq. (14.150), the total energy $E_{T_{ethane}}\left(CH_3\right)$ of the CH_3 MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{ethane}2sp^3$ HO and the three H_2-type ellipsoidal MOs that forms the CH_3 MO as given by Eq. (13.540). Using Eq. (13.431), $E_{T_{ethane}}\left(CH_3\right)$ is given by

$$\begin{aligned} E_{T_{ethane}}\left(CH_3\right) &= E_T + E\left(C_{ethane},2sp^3\right) \\ &= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV \end{aligned} \tag{14.174}$$

$E_{T_{ethane}}\left(CH_3\right)$ given by Eq. (14.174) is set equal to three times the energy of the H_2-type ellipsoidal MO minus two times the Coulombic energy of H given by Eq. (13.542):

$$E_T\left(CH_3\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV = -67.69450\ eV \tag{14.175}$$

From the energy relationship given by Eq. (14.175) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH_3 MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.175) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e52.33505 \tag{14.176}$$

The most convenient way to solve Eq. (14.176) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.64469a_0 = 8.70331\ X\ 10^{-11}\ m \tag{14.177}$$

Substitution of Eq. (14.177) into Eq. (14.60) gives

$$c' = 1.04712a_0 = 5.54111\ X\ 10^{-11}\ m \tag{14.178}$$

The internuclear distance given by multiplying Eq. (14.178) by two is

$$2c' = 2.09424a_0 = 1.10822\ X\ 10^{-10}\ m \tag{14.179}$$

The experimental bond distance is [3]

$$2c' = 1.0940\ X\ 10^{-10}\ m \tag{14.180}$$

Substitution of Eqs. (14.177-14.178) into Eq. (14.62) gives

$$b = c = 1.26828a_0 = 6.71145\ X\ 10^{-11}\ m \tag{14.181}$$

Substitution of Eqs. (14.177-14.178) into Eq. (14.63) gives

$$e = 0.63667 \tag{14.182}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{ethane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{ethane2sp^3} = 0.87495a_0$ is the radius of the $C_{ethane}2sp^3$ shell. Substitution of Eqs. (14.177-14.178) into Eq. (13.261) gives

$$\theta' = 79.34° \tag{14.183}$$

Then, the angle $\theta_{C-H_{ethane}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-H_{ethane}2sp^3HO} = 180° - 79.34° = 100.66° \tag{14.184}$$

as shown in Figure 38.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C-H_{ethane},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C_{ethane}2sp^3$ radial vector obeys the following relationship:

$$r_{ethane2sp^3}\sin\theta_{C-H_{ethane}2sp^3HO} = 0.87495a_0\sin\theta_{C-H_{ethane}2sp^3HO} = b\sin\theta_{C-H_{ethane},H_2MO} \tag{14.185}$$

such that

$$\theta_{C-H_{ethane},H_2MO} = \sin^{-1}\frac{0.87495a_0\sin\theta_{C-H_{ethane}2sp^3HO}}{b} = \sin^{-1}\frac{0.87495a_0\sin 100.66°}{b} \tag{14.186}$$

with the use of Eq. (14.184). Substitution of Eq. (14.181) into Eq. (14.186) gives

$$\theta_{C-H_{ethane},H_2MO} = 42.68° \tag{14.187}$$

Then, the distance d_{C-H_{ethane},H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{ethane},H_2MO} = a\cos\theta_{C-H_{ethane},H_2MO} \tag{14.188}$$

Substitution of Eqs. (14.177) and (14.187) into Eq. (14.188) gives

$$d_{C-H_{ethane},H_2MO} = 1.20901a_0 = 6.39780\,X\,10^{-11}\ m \tag{14.189}$$

The distance $d_{C-H_{ethane}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{ethane}2sp^3HO} = d_{C-H_{ethane},H_2MO} - c' \tag{14.190}$$

Substitution of Eqs. (14.178) and (14.189) into Eq. (14.190) gives

$$d_{C-H_{ethane}2sp^3HO} = 0.16189a_0 = 8.56687\,X\,10^{-12}\ m \tag{14.191}$$

BOND ANGLE OF THE CH_3 GROUPS

Each CH_3 MO comprises a linear combination of three $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a H_2-type ellipsoidal MO and the $C_{ethane}2sp^3$ HO. A bond is also possible between the two H atoms of the $C-H$ bonds. Such $H-H$ bonding would decrease the $C-H$ bond strength since electron density would be shifted from the $C-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $C-H$ bonds is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal H atoms of the $C-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.192}$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.193}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (14.62).

The bond angle of the CH_3 groups of ethane is derived by using the orbital composition and an energy matching factor as in the case with the CH_3 radical. Since the two H_2-type ellipsoidal MOs initially comprise 75% of the H electron density of H_2 and the energy of each H_2-type ellipsoidal MO is matched to that of the $C_{ethane}2sp^3$ HO, the component energies and the total energy E_T of the $H-H$ bond are given by Eqs. (13.67-13.73) except that V_e, T, and V_m are corrected for the hybridization-energy-matching factor

of 0.87495. Hybridization with 25% electron donation to the $C-C$-bond gives rise to the $C_{ethane}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{ethane},2sp^3\right)$ given by Eq. (14.149). The corresponding normalization factor for determining the zero of the total $H-H$ bond energy is given by the ratio of 15.55033 eV, the magnitude of $E_{Coulomb}\left(C_{ethane},2sp^3\right)$ given by Eq. (14.149), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The hybridization energy factor $C_{ethaneC2sp^3HO}$ is

$$C_{ethaneC2sp^3HO}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}}}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.87495 a_0}}=\frac{13.605804\ eV}{15.55033\ eV}=0.87495 \tag{14.194}$$

Substitution of Eq. (14.152) into Eq. (13.233) with the hybridization factor of 0.87495 gives

$$0=\left[\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[(0.87495)^{-1}\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right]\right]$$
$$+\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o a^3}-\frac{e^2}{8\pi\varepsilon_o\left(a+c'\right)^3}}{0.5m_p}}\Bigg] \tag{14.195}$$

From the energy relationship given by Eq. (14.195) and the relationship between the axes given by Eqs. (14.192-14.193) and (14.62-14.63), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (14.195) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=5.7000a_0=3.0163\ X\ 10^{-10}\ m \tag{14.196}$$

Substitution of Eq. (14.196) into Eq. (14.192) gives

$$c'=1.6882a_0=8.9335\ X\ 10^{-11}\ m \tag{14.197}$$

The internuclear distance given by multiplying Eq. (14.197) by two is

$$2c'=3.3764a_0=1.7867\ X\ 10^{-10}\ m \tag{14.198}$$

Substitution of Eqs. (14.196-14.197) into Eq. (14.62) gives

$$b=c=5.4443a_0=2.8810\ X\ 10^{-10}\ m \tag{14.199}$$

Substitution of Eqs. (14.196-14.197) into Eq. (14.63) gives

$$e = 0.2962 \tag{14.200}$$

From, $2c'_{H-H}$ (Eq. (14.198)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (14.195)), and $2c'_{C-H}$ (Eq. (14.179)), the internuclear distance of each $C-H$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle θ between the $C-H$ bonds is

$$\theta = \cos^{-1}\left(\frac{2(2.09424)^2 - (3.3764)^2}{2(2.09424)^2}\right) = \cos^{-1}(-0.29964) = 107.44^\circ \tag{14.201}$$

The experimental angle between the $C-H$ bonds is [8]

$$\theta = 107.4^\circ \tag{14.202}$$

The CH_3 radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance $d_{origin-H}$ from the origin to the nucleus of a hydrogen atom given by Eqs. (14.198) and (13.412) is

$$d_{origin-H} = 1.94936a_0 \tag{14.203}$$

The height along the z-axis of the pyramid from the origin to C nucleus d_{height} given by Eqs. (13.414), (14.179), and (14.203) is

$$d_{height} = 0.76540a_0 \tag{14.204}$$

The angle θ_v of each $C-H$ bond from the z-axis given by Eqs. (13.416), (14.203), and (14.204) is

$$\theta_v = 68.563^\circ \tag{14.205}$$

The $C-C$ bond is along the z-axis. Thus, the bond angle θ_{C-C-H} between the internuclear axis of the $C-C$ bond and a H atom of the methyl groups is given by

$$\theta_{C-C-H} = 180 - \theta_v \tag{14.206}$$

Substitution of Eq. (14.205) into Eq. (14.206) gives

$$\theta_{C-C-H} = 111.44^\circ \tag{14.207}$$

The experimental angle between the $C-C-H$ bonds is [3]

$$\theta_{C-C-H} = 111.17^\circ \tag{14.208}$$

The CH_3CH_3 MO shown in Figure 39 was rendered using these parameters. A minimum energy is obtained with a staggered configuration consistent with observations [3].

The charge-density in the $C-C$-bond MO is increased by a factor of 0.25 with the formation of the $C_{ethane}2sp^3$ HOs each having a smaller radius. Using the orbital composition of the CH_3 groups (Eq. (14.173)) and the $C-C$-bond MO (Eq. (14.139), the radii of $C1s=0.17113a_0$ (Eq. (10.51)) and $C_{ethane}2sp^3=0.87495a_0$ (Eq. (14.148)) shells, and the parameters of the $C-C$-bond (Eqs. (13.3-13.4), (14.158-14.160), and (14.162-14.172)), the parameters of the $C-H$-bond MOs (Eqs. (13.3-13.4), (14.177-14.179), and (14.181-14.191)), and the bond-angle parameters (Eqs. (14.195-14.208)), the charge-density of the CH_3CH_3 MO comprising the linear combination of two sets of three $C-H$-bond MOs and a $C-C$-bond MO bridging the two methyl groups is shown in Figure 39. Each $C-H$-bond MO comprises a H_2-type ellipsoidal MO and a $C_{ethane}2sp^3$ HO having the dimensional diagram shown in Figure 38. The $C-C$-bond MO comprises a H_2-type ellipsoidal MO bridging two $C_{ethane}2sp^3$ HOs having the dimensional diagram shown in Figure 37.

ENERGIES OF THE CH_3 GROUPS

The energies of each CH_3 group of ethane are given by the substitution of the semiprincipal axes (Eqs. (14.177-14.178) and (14.181)) into the energy equations of the methyl radical (Eqs. (13.556-13.560)), with the exception that $E\left(C_{ethane},2sp^3\right)$ replaces $E\left(C,2sp^3\right)$ in Eq. (13.560):

$$V_e=3(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-107.68424\ eV \tag{14.209}$$

$$V_p=\frac{3e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=38.98068\ eV \tag{14.210}$$

$$T=3(0.91771)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=32.73700\ eV \tag{14.211}$$

$$V_m=3(0.91771)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-16.36850\ eV \tag{14.212}$$

$$E_{T_{ethane}}(CH_3)=-\frac{3e^2}{8\pi\varepsilon_0c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV=-67.69451\ eV \tag{14.213}$$

where $E_{T_{ethane}}(CH_3)$ is given by Eq. (14.174) which is reiteratively matched to Eq. (13.542) within five-significant-figure round off error.

VIBRATION OF THE $^{12}CH_3$ GROUPS

The vibrational energy levels of CH_3 in ethane may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $^{12}CH_3$ GROUPS

The equations of the radiation reaction force of the methyl groups in ethane are the same as those of the methyl radical with the substitution of the methyl-group parameters. Using Eq. (13.561), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.50664\,X\,10^{16}\ rad/s \tag{14.214}$$

where b is given by Eq. (14.181). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.50664\,X\,10^{16}\ rad/s = 16.49915\ eV \tag{14.215}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.215) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(16.49915\ eV)}{m_e c^2}} = -0.25422\ eV \tag{14.216}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH_3 due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.216) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which

is 1/2 of the vibrational energy of each $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having three independent bonds, $\overline{E}'_{ethane\ osc}\left({}^{12}CH_3\right)$ per bond is

$$\overline{E}'_{ethane\ osc}\left({}^{12}CH_3\right)=\overline{E}_D+\overline{E}_{Kvib}=\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.217}$$

$$\overline{E}'_{ethane\ osc}\left({}^{12}CH_3\right)=-0.25422\ eV+\frac{1}{2}(0.35532\ eV)=-0.07656\ eV \tag{14.218}$$

Given that the vibration and reentrant oscillation is for three $C-H$ bonds, $\overline{E}_{ethane\ osc}\left({}^{12}CH_3\right)$, is:

$$\begin{aligned}\overline{E}_{ethane\ osc}\left({}^{12}CH_3\right)&=3\left(\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\&=3\left(-0.25422\ eV+\frac{1}{2}(0.35532\ eV)\right)\\&=-0.22967\ eV\end{aligned} \tag{14.219}$$

TOTAL AND DIFFERENCE ENERGIES OF THE ${}^{12}CH_3$ GROUPS

$E_{ethaneT+osc}\left({}^{12}CH_3\right)$, the total energy of each ${}^{12}CH_3$ group including the Doppler term, is given by the sum of $E_{T_{ethane}}\left(CH_3\right)$ (Eq. (14.213)) and $\overline{E}_{ethane\ osc}\left({}^{12}CH_3\right)$ given by Eq. (14.219):

$$\begin{aligned}E_{ethaneT+osc}\left(CH_3\right)&=V_e+T+V_m+V_p+E\left(C_{ethane},2sp^3\right)+\overline{E}_{ethane\ osc}\left({}^{12}CH_3\right)\\&=E_{T_{ethane}}\left(CH_3\right)+\overline{E}_{ethane\ osc}\left({}^{12}CH_3\right)\end{aligned} \tag{14.220}$$

$$\begin{aligned}E_{ethaneT+osc}\left({}^{12}CH_3\right)&=\left\{\begin{array}{l}\left(\frac{-3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.359469\ eV\right)\\-3\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}}{m_e}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\}\\&=-67.69450\ eV-3\left(0.25422\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{14.221}$$

From Eqs. (14.217-14.221), the total energy of each ${}^{12}CH_3$ is

$$E_{ethaneT+osc}\left({}^{12}CH_3\right) = -67.69450\ eV + \overline{E}_{ethane\ osc}\left({}^{12}CH_3\right)$$
$$= -67.69450\ eV - 3\left(0.25422\ eV - \frac{1}{2}(0.35532\ eV)\right) \qquad (14.222)$$
$$= -67.92417\ eV$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The total energy for each methyl radical given by Eq. (13.569) is

$$E_{radicalT+osc}\left({}^{12}CH_3\right) = -67.69450\ eV + \overline{E}_{radical\ osc}\left({}^{12}CH_3\right)$$
$$= -67.69450\ eV - 3\left(0.25670\ eV - \frac{1}{2}(0.35532\ eV)\right) \qquad (14.223)$$
$$= -67.93160\ eV$$

The difference in energy between the methyl groups and the methyl radical $\Delta E_{T+osc}\left({}^{12}CH_3\right)$ is given by two times the difference between Eqs. (14.222) and (14.223):

$$\Delta E_{T+osc}\left({}^{12}CH_3\right) = 2\left(E_{ethaneT+osc}\left({}^{12}CH_3\right) - E_{radicalT+osc}\left({}^{12}CH_3\right)\right)$$
$$= 2\left(-67.92417\ eV - \left(-67.93160\ eV\right)\right) \qquad (14.224)$$
$$= 0.01487\ eV$$

SUM OF THE ENERGIES OF THE $C-C$ σ MO AND THE HOs OF ETHANE

The energy components of V_e, V_p, T, V_m, and E_T of the $C-C$-bond MO are the same as those of the CH MO as well as each $C-H$-bond MO of the methyl groups except that energy of the $C_{ethane}2sp^3$ HO is used. The energies of each $C-C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.158-14.159) and (14.162)) into the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that $E\left(C_{ethane}, 2sp^3\right)$ replaces $E\left(C, 2sp^3\right)$ in Eq. (13.453):

$$V_e = (0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -29.101124\ eV \qquad (14.225)$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 9.37273\ eV \qquad (14.226)$$

$$T = (0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 6.90500\ eV \qquad (14.227)$$

$$V_m = (0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -3.45250\ eV \tag{14.228}$$

$$E_T(C-C,\sigma) = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV = -31.63535\ eV \tag{14.229}$$

where $E_T(C-C,\sigma)$ is the total energy of the $C-C$ σ MO given by Eq. (14.155) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C-C$-bond MO, $E_T(C-C)$, is given by the sum of two times $E_T(C-C,2sp^3)$, the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of the $C-C$-bond MO (Eq. (14.151)), and $E_T(C-C,\sigma)$, the σ MO contribution given by Eq. (14.156):

$$\begin{aligned} E_T(C-C) &= 2E_T(C-C,2sp^3)+E_T(C-C,\sigma) \\ &= \left(\begin{array}{l} 2(-0.72457\ eV)+ \\ \left(-\frac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right]-15.35946\ eV\right) \end{array}\right) \\ &= 2(-0.72457\ eV)+(-31.63537\ eV) \\ &= -33.08452\ eV \end{aligned} \tag{14.230}$$

VIBRATION OF ETHANE

The vibrational energy levels of CH_3CH_3 may be solved as two sets of three equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $C-C$-BOND MO OF ETHANE

The equations of the radiation reaction force of the symmetrical $C-C$-bond MO are given by Eqs. (11.231-11.233), except the force-constant factor is 0.5 based on the force constant k' of Eq. (14.152), and the $C-C$-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.5e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 9.55643\,X\,10^{15}\ rad/s \tag{14.231}$$

where a is given by Eq. (14.158). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 9.55643\,X\,10^{15}\ rad/s = 6.29021\ eV \tag{14.232}$$

In Eq. (11.181), substitution of $E_T(C-C)$ (Eq. (14.230)) for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.232) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -33.08450\ eV\sqrt{\frac{2e(6.29021\ eV)}{m_e c^2}} = -0.16416\ eV \tag{14.233}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $C-C$-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.233) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C-C$ bond. Using the experimental $C-C$ $E_{vib}(\upsilon_3)$ of $993\ cm^{-1}$ $(0.12312\ eV)$ [10] for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{osc}(C-C,\sigma)$ is

$$\overline{E}_{osc}(C-C,\sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.234}$$

$$\overline{E}_{osc}(C-C,\sigma) = -0.16416\ eV + \frac{1}{2}(0.12312\ eV) = -0.10260\ eV \tag{14.235}$$

TOTAL ENERGIES OF THE $C-C$-BOND MO OF ETHANE

$E_{T+osc}(C-C)$, the total energy of the $C-C$-bond MO including the Doppler term, is given by the sum of $E_T(C-C)$ (Eq. (14.230)) and $\overline{E}_{osc}(C-C,\sigma)$ given by Eq. (14.235):

$$E_{T+osc}(C-C) = V_e + T + V_m + V_p + E\left(C_{ethane}, 2sp^3\right) + 2E_T\left(C-C, 2sp^3\right) + \overline{E}_{osc}(C-C,\sigma)$$
$$= E_T(C-C,\sigma) + 2E_T\left(C-C, 2sp^3\right) + \overline{E}_{osc}(C-C,\sigma)$$
$$= E_T(C-C) + \overline{E}_{osc}(C-C,\sigma) \tag{14.236}$$

$$E_{T+osc}(C-C) = \left\{\begin{array}{l}\left(\frac{-e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.35946\ eV+2E_T\left(C-C,2sp^3\right)\right) \\ \left(1+\sqrt{\frac{2\hbar\sqrt{\frac{1}{2}\frac{e^2}{4\pi\varepsilon_o a^3}m_e}}{m_e c^2}}\right)+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\end{array}\right\}$$
$$= -33.08452\ eV - 0.16416\ eV + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.237}$$

From Eqs. (14.234-14.237), the total energy of the $C-C$-bond MO is

$$E_{T+osc}(C-C) = -31.63537\ eV + 2E_T\left(C-C,2sp^3\right) + \overline{E}_{osc}(C-C,\sigma)$$
$$= -31.63537\ eV + 2(-0.72457\ eV) - 0.16416\ eV + \frac{1}{2}(0.12312\ eV) \tag{14.238}$$
$$= -33.18712\ eV$$

where the experimental E_{vib} was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

BOND ENERGY OF THE $C-C$ BOND OF ETHANE

The dissociation energy of the $C-C$ bond of CH_3CH_3, $E_D(H_3C-CH_3)$, is given by two times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of the $C2sp^3$ HO of each CH_3 radical that bond with a single $C-C$ bond, minus the sum of $\Delta E_{T+osc}\left({}^{12}CH_3\right)$ (Eq. (14.224)), the energy change going from the methyl radicals to the methyl groups of ethane, and $E_{T+osc}(C-C)$ (Eq. (14.238)). Thus, the dissociation energy of the $C-C$ bond of CH_3CH_3, is

$$E_D(H_3C-CH_3) = 2\left(E\left(C,2sp^3\right)\right) - \left(\Delta E_{T+osc}\left({}^{12}CH_3\right) + E_{T+osc}(C-C)\right)$$
$$= 2(-14.63489\ eV) - (0.01487\ eV - 33.18712\ eV)$$
$$= 2(-14.63489\ eV) - (33.17225\ eV) \tag{14.239}$$
$$= 3.90247\ eV$$

The experimental dissociation energy of the $C-C$ bond of CH_3CH_3 is [6]

$$E_D\left(H_3C-CH_3\right)=3.89690\ eV \tag{14.240}$$

The results of the determination of bond parameters of CH_3CH_3 are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

ETHYLENE MOLECULE (CH_2CH_2)

The ethylene molecule CH_2CH_2 is formed by the reaction of two dihydrogen carbide radicals:

$$CH_2+CH_2\rightarrow CH_2CH_2 \tag{14.241}$$

CH_2CH_2 can be solved using the same principles as those used to solve the methane series $CH_{n=1,2,3,4}$, wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of two H atomic orbitals (AOs) combine with two sets of two carbon $2sp^3$ HOs to form two dihydrogen carbide groups comprising a linear combination of four diatomic H_2-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two CH_2 groups bond by forming a H_2-type MO between the remaining two $C2sp^3$ HOs on each carbon atom.

FORCE BALANCE OF THE $C=C$-BOND MO OF ETHYLENE

CH_2CH_2 comprises a chemical bond between two CH_2 radicals wherein each radical comprises two chemical bonds between carbon and hydrogen atoms. The solution of the parameters of CH_2 is given in the Dihydrogen Carbide (CH_2) section. Each $C-H$ bond of CH_2 having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% H_2-type ellipsoidal MO and 25% $C2sp^3$ HO. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H_2, each of

the two $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the CH_2 MO that has the symmetry of an s orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

Two CH_2 radicals bond to form CH_2CH_2 by forming a MO between the two pairs of remaining $C2sp^3$-HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between four $C2sp^3$ HOs to form a molecular orbital (MO) comprising four spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy.

As in the case of the $C-H$ bonds, the $C=C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each C atom. The energy of the H_2-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of OH, NH, CH, the $C=O$-bond MO of CO_2, and the $C-C$-bond MO of CH_3CH_3, the $C=C$-bond MO of ethylene must comprise 75% of a H_2-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C=C$-bond MO must comprise a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$2\left(2\ C2sp^3+0.75\ H_2\ MO\right)\rightarrow C=C-bond\ MO \tag{14.242}$$

The linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C=C$-

bond MO to achieve an energy minimum. The force balance of the $C=C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.242) and the energy matching condition between the $C2sp^3$-HO components of the MO.

Similarly, the energies of each CH_2 MO involve each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the H_2-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. This energy is determined by the considering the effect of the donation of 25% electron density from the two pairs of $C2sp^3$ HOs to the $C=C$-bond MO with the formation of the $C_{ethylene}2sp^3$ HOs each having a smaller radius. The $2sp^3$ hybridized orbital arrangement is given by Eq. (14.140). The sum $E_T\left(C,2sp^3\right)$ of calculated energies of C, C^+, C^{2+}, and C^{3+} is given by Eq. (14.141). The radius r_{2sp^3} of the $C2sp^3$ shell is given by Eq. (14.142). The Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ and the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell are given by Eqs. (14.143) and (14.146), respectively.

Next, consider the formation of the $C=C$-bond MO of ethylene from two CH_2 radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C_{ethylene},2sp^3\right)$ of calculated energies of $C2sp^3$, C^+, C^{2+}, and C^{3+} from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned}E_T\left(C_{ethylene},2sp^3\right)&=-\left(64.3921\ eV+48.3125\ eV+24.2762\ eV+E\left(C,2sp^3\right)\right)\\&=-\left(64.3921\ eV+48.3125\ eV+24.2762\ eV+14.63489\ eV\right)\\&=-151.61569\ eV\end{aligned}$$

(14.243)

where $E\left(C,2sp^3\right)$ (Eq. (14.146)) is the sum of the energy of C, $-11.27671\ eV$, and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the $E_T\left(C_{ethylene},2sp^3\right)$ is purely Coulombic.

The sharing of electrons between two pairs of $C2sp^3$ HOs to form a $C=C$-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating

$C2sp^3$ HO donates an excess of 25% per bond of its electron density to the $C=C$ -bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethylene2sp^3}$ of the $C2sp^3$ shell of ethylene may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{ethylene2sp^3}=\left(\sum_{n=2}^{5}(Z-n)-0.5\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)}=\frac{9.5e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)}=0.85252a_0 \tag{14.244}$$

where $Z=6$ for carbon. Using Eqs. (10.102) and (14.244), the Coulombic energy $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E_{Coulomb}\left(C_{ethylene},2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.85252a_0}=-15.95955\ eV \tag{14.245}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.245), the energy $E\left(C_{ethylene},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$\begin{aligned}E\left(C_{ethylene},2sp^3\right)&=\frac{-e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}\\&=-15.95955\ eV+0.19086\ eV\\&=-15.76868\ eV\end{aligned} \tag{14.246}$$

Thus, $E_T\left(C=C,2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C=C$ -bond MO is given by the difference between Eq. (14.146) and Eq. (14.246):

$$\begin{aligned}E_T\left(C=C,2sp^3\right)&=E\left(C_{ethylene},2sp^3\right)-E\left(C,2sp^3\right)\\&=-15.76868\ eV-\left(-14.63489\ eV\right)\\&=-1.13380\ eV\end{aligned} \tag{14.247}$$

As in the case of Cl_2, each H_2-type ellipsoidal MO comprises 75% of the $C=C$ -bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to each bond of the $C=C$ -bond MO causes the electron charge density in Eq. (11.65) to be is given by $\frac{-e}{2}=-0.5e$. The

corresponding force constant k' is given by Eq. (14.152). In addition, the energy matching at both $C2sp^3$ HOs further requires that k' be corrected by the hybridization factor given by Eq. (13.430). Thus, the force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci (Eq. (11.65)) is given by

$$k' = C_{C2sp^3HO}\frac{(0.5)2e^2}{4\pi\varepsilon_0} = 0.91771\frac{(0.5)2e^2}{4\pi\varepsilon_0} \tag{14.248}$$

The distance from the origin to each focus c' is given by substitution of Eq. (14.248) into Eq. (13.60). Thus, the distance from the origin of the component of the double $C=C$-bond MO to each focus c' is given by

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{(0.91771)m_e e^2 a}} = \sqrt{\frac{aa_0}{0.91771}} \tag{14.249}$$

The internuclear distance from Eq. (14.249) is

$$2c' = 2\sqrt{\frac{aa_0}{0.91771}} \tag{14.250}$$

The length of the semiminor axis of the prolate spheroidal $C=C$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C=C$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C=C$-bond MO are solved.

The general equations for the energy components of V_e, V_p, T, V_m, and E_T of the $C=C$-bond MO are the same as those of the CH MO except that energy of the $C_{ethylene}2sp^3$ HO is used and the double-bond nature is considered. In the case of a single bond, the prolate spheroidal H_2-type MO transitions to the $C_{ethylene}2sp^3$ HO of each carbon, and the energy of the $C_{ethylene}2sp^3$ shell must remain constant and equal to the $E\left(C_{ethylene},2sp^3\right)$ given by Eq. (14.246). Thus, the energy $E\left(C_{ethylene},2sp^3\right)$ in Eq. (14.246) adds to that of the energies of the corresponding H_2-type ellipsoidal MO. The second bond of the double $C=C$-bond MO also transitions to the $C_{ethylene}2sp^3$ HO of each C. The energy of a second H_2-type ellipsoidal MO adds to the first energy component, and the two bonds achieve an energy minimum as a linear combination of the two H_2-type ellipsoidal MOs each having the carbon nuclei as the foci. Each $C-C$-bond MO comprises the same $C_{ethylene}2sp^3$ HO shells of

constant energy given by Eq. (14.246). As in the case of the water, NH_2, and ammonia molecules given by Eqs. (13.180), (13.320), and (13.372), respectively, the energy of the redundant shell is subtracted from the total energy of the linear combination of the σ MO. Thus, the total energy $E_T(C=C,\sigma)$ of the σ component of the $C=C$ -bond MO is given by the sum of the energies of the two bonds each comprising the linear combination of the $C_{ethylene}2sp^3$ HO and the H_2-type ellipsoidal MO as given by Eq. (14.242) wherein the E_T terms add positively, the $E(C_{ethylene},2sp^3)$ terms cancel, and the energy matching condition between the components is provided by Eq. (14.248). Using Eqs. (13.431) and (14.246), $E_T(C=C,\sigma)$ is given by

$$\begin{aligned} E_T(C=C,\sigma) &= E_T + E(C_{ethylene},2sp^3) - E(C_{ethylene},2sp^3) \\ &= -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \end{aligned} \tag{14.251}$$

The total energy term of the double $C=C$ -bond MO is given by the sum of the two H_2-type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition, $E_T(C=C,\sigma)$ given by Eq. (14.251) is set equal to two times Eq. (13.75):

$$E_T(C=C,\sigma) = -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] = -63.27074\ eV \tag{14.252}$$

From the energy relationship given by Eq. (14.252) and the relationship between the axes given by Eqs. (14.249-14.250) and (13.62-13.63), the dimensions of the $C=C$ -bond MO can be solved.

Substitution of Eq. (14.249) into Eq. (14.252) gives

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{0.91771}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{0.91771}}}{a-\sqrt{\frac{aa_0}{0.91771}}}-1\right] = e63.27074 \tag{14.253}$$

The most convenient way to solve Eq. (14.253) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.47228a_0 = 7.79098\ X\ 10^{-11}\ m \tag{14.254}$$

Substitution of Eq. (14.254) into Eq. (14.249) gives

$$c' = 1.26661a_0 = 6.70259\ X\ 10^{-11}\ m \tag{14.255}$$

The internuclear distance given by multiplying Eq. (14.255) by two is

$$2c' = 2.53321a_0 = 1.34052\,X\,10^{-10}\ m \tag{14.256}$$

The experimental bond distance is [3]

$$2c' = 1.339\,X\,10^{-10}\ m \tag{14.257}$$

Substitution of Eqs. (14.254-14.255) into Eq. (13.62) gives

$$b = c = 0.75055a_0 = 3.97173\,X\,10^{-11}\ m \tag{14.258}$$

Substitution of Eqs. (14.252-14.255) into Eq. (13.63) gives

$$e = 0.86030 \tag{14.259}$$

The nucleus of the C atoms comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{ethylene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{ethylene2sp^3} = 0.85252a_0$ is the radius of the $C_{ethylene}2sp^3$ shell. Substitution of Eqs. (14.254-14.255) into Eq. (13.261) gives

$$\theta' = 129.84° \tag{14.260}$$

Then, the angle $\theta_{C=C_{ethylene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C=C_{ethylene}2sp^3HO} = 180° - 129.84° = 50.16° \tag{14.261}$$

as shown in Figure 40.

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C=C_{ethylene},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with each $C_{ethylene}2sp^3$ radial vector obeys the following relationship:

$$r_{ethylene2sp^3}\sin\theta_{C=C_{ethylene}2sp^3HO} = 0.85252a_0\sin\theta_{C=C_{ethylene}2sp^3HO} = b\sin\theta_{C=C_{ethylene},H_2MO} \tag{14.262}$$

such that

$$\theta_{C=C_{ethylene},H_2MO} = \sin^{-1}\frac{0.85252a_0\sin\theta_{C=C_{ethylene}2sp^3HO}}{b} = \sin^{-1}\frac{0.85252a_0\sin 50.16°}{b} \tag{14.263}$$

with the use of Eq. (14.261). Substitution of Eq. (14.258) into Eq. (14.263) gives

$$\theta_{C=C_{ethylene},H_2MO} = 60.70° \tag{14.264}$$

Then, the distance $d_{C=C_{ethylene},H_2MO}$ along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C=C_{ethylene},H_2MO} = a\cos\theta_{C=C_{ethylene},H_2MO} \tag{14.265}$$

Substitution of Eqs. (14.254) and (14.264) into Eq. (14.265) gives

$$d_{C=C_{ethylene},H_2MO} = 0.72040a_0 = 3.81221\,X\,10^{-11}\ m \tag{14.266}$$

The distance $d_{C=C_{ethylene}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C=C_{ethylene}2sp^3HO} = c' - d_{C=C_{ethylene},H_2MO} \tag{14.267}$$

Substitution of Eqs. (14.255) and (14.266) into Eq. (14.267) gives

$$d_{C=C_{ethylene}2sp^3HO} = 0.54620a_0 = 2.89038\,X\,10^{-11}\ m \tag{14.268}$$

FORCE BALANCE OF THE CH_2 MOs OF ETHYLENE

Each of the two equivalent CH_2 MOs must comprise two $C-H$ bonds with each comprising 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.494):

$$2\left[1\,C2sp^3 + 0.75\,H_2\,MO\right] \rightarrow CH_2\,MO \tag{14.269}$$

The force balance of the CH_2 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.494) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH_2 MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the CH_2 MO are solved.

Consider the formation of the double $C=C$-bond MO of ethylene from two CH_2 radicals, each having a $C2sp^3$ shell with an energy given by Eq. (14.146). The energy

components of V_e, V_p, T, V_m, and E_T are the same as those of the dihydrogen carbide radical, two times those of CH corresponding to the two $C-H$ bonds, except that two times $E_T\left(C=C,2sp^3\right)$ is subtracted from $E_T\left(CH_2\right)$ of Eq. (13.495). The subtraction of the energy change of the $C2sp^3$ shells with the formation of the $C=C$-bond MO matches the energy of the $C-H$-bond MOs to the decrease in the energy of the $C2sp^3$ HOs. Using Eqs. (13.495) and (14.247), $E_{T_{ethylene}}\left(CH_2\right)$ is given by

$$E_{T_{ethylene}}\left(CH_2\right)=E_T+E\left(C,2sp^3\right)-2E_T\left(C=C,2sp^3\right)$$
$$=\begin{pmatrix}-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-(-2.26758\ eV)\end{pmatrix} \tag{14.270}$$

$E_{T_{ethylene}}\left(CH_2\right)$ given by Eq. (14.270) is set equal to two times the energy of the H_2-type ellipsoidal MO minus the Coulombic energy of H given by Eq. (13.496):

$$E_{T_{ethylene}}\left(CH_2\right)=\begin{pmatrix}-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-(-2.26758\ eV)\end{pmatrix}=-49.66493\ eV \tag{14.271}$$

From the energy relationship given by Eq. (14.271) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH_2 MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.271) gives

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e37.29762 \tag{14.272}$$

The most convenient way to solve Eq. (14.272) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.56946a_0=8.30521\ X\ 10^{-11}\ m \tag{14.273}$$

Substitution of Eq. (14.273) into Eq. (13.60) gives

$$c'=1.02289a_0=5.41290\ X\ 10^{-11}\ m \tag{14.274}$$

The internuclear distance given by multiplying Eq. (14.274) by two is

$$2c'=2.04578a_0=1.08258\ X\ 10^{-10}\ m \tag{14.275}$$

The experimental bond distance is [3]

$$2c' = 1.087\,X\,10^{-10}\ m \tag{14.276}$$

Substitution of Eqs. (14.273-14.274) into Eq. (14.62) gives

$$b = c = 1.19033a_0 = 6.29897\,X\,10^{-11}\ m \tag{14.277}$$

Substitution of Eqs. (14.273-14.274) into Eq. (14.63) gives

$$e = 0.65175 \tag{14.278}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{ethylene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{ethylene2sp^3} = 0.85252a_0$ is the radius of the $C_{etthylene}2sp^3$ shell. Substitution of Eqs. (14.273-14.274) into Eq. (13.261) gives

$$\theta' = 84.81° \tag{14.279}$$

Then, the angle $\theta_{C-H_{ethylene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-H_{ethylene}2sp^3HO} = 180° - 84.81° = 95.19° \tag{14.280}$$

as shown in Figure 41.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C-H_{ethylene},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C_{ethylene}2sp^3$ radial vector obeys the following relationship:

$$r_{ethylene2sp^3}\sin\theta_{C-H_{ethylene}2sp^3HO} = 0.85252a_0\sin\theta_{C-H_{ethylene}2sp^3HO} = b\sin\theta_{C-H,H_2MO} \tag{14.281}$$

such that

$$\theta_{C-H_{ethylene},H_2MO} = \sin^{-1}\frac{0.85252a_0\sin\theta_{C-H_{ethylene}2sp^3HO}}{b} = \sin^{-1}\frac{0.85252a_0\sin 95.19°}{b} \tag{14.282}$$

with the use of Eq. (14.280). Substitution of Eq. (14.277) into Eq. (14.282) gives

$$\theta_{C-H_{ethylene},H_2MO} = 45.50° \tag{14.283}$$

Then, the distance $d_{C-H_{ethylene},H_2MO}$ along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{ethylene},H_2MO} = a\cos\theta_{C-H_{ethylene},H_2MO} \tag{14.284}$$

Substitution of Eqs. (14.273) and (14.283) into Eq. (14.284) gives

$$d_{C-H_{ethylene},H_2MO} = 1.10002a_0 = 5.82107\,X\,10^{-11}\ m \tag{14.285}$$

The distance $d_{C-H_{ethylene}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{ethylene}2sp^3HO} = d_{C-H_{ethylene},H_2MO} - c' \tag{14.286}$$

Substitution of Eqs. (14.274) and (14.285) into Eq. (14.286) gives

$$d_{C-H_{ethylene}2sp^3HO} = 0.07713a_0 = 4.08171\,X\,10^{-12}\ m \tag{14.287}$$

BOND ANGLE OF THE CH_2 GROUPS

Each CH_2 MO comprises a linear combination of two $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a H_2-type ellipsoidal MO and the $C_{ethylene}2sp^3$ HO. A bond is also possible between the two H atoms of the $C-H$ bonds. Such $H-H$ bonding would decrease the $C-H$ bond strength since electron density would be shifted from the $C-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $C-H$ bonds is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal H atoms of the $C-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.288}$$

The internuclear distance from Eq. (13.229) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.289}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (14.62).

The bond angle of the CH_2 groups of ethane is derived by using the orbital composition and an energy matching factor as in the case with the dihydrogen carbide radical and the CH_3 groups of ethane. Since the two H_2-type ellipsoidal MOs initially comprise 75% of the H electron density of H_2 and the energy of each H_2-type ellipsoidal MO is matched to that of the $C_{ethylene}2sp^3$ HO, the component energies and the total energy E_T of the

$H-H$ bond are given by Eqs. (13.67-13.73) except that V_e, T, and V_m are corrected for the hybridization-energy-matching factor of 0.85252. Hybridization with 25% electron donation to the $C=C$-bond gives rise to the $C_{ethylene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ given by Eq. (14.245). The corresponding normalization factor for determining the zero of the total $H-H$ bond energy is given by the ratio of 15.95955 eV, the magnitude of $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ given by Eq. (14.245), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The hybridization energy factor $C_{ethyleneC2sp^3HO}$ is

$$C_{ethyleneC2sp^3HO}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}}}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.85252 a_0}}=\frac{13.605804\ eV}{15.95955\ eV}=0.85252 \quad (14.290)$$

Substitution of Eq. (14.290) into Eq. (13.233) or Eq. (14.195) with the hybridization factor of 0.85252 gives

$$0=\left[\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[(0.85252)^{-1}\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}}\right]\right]$$
$$+\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o a^3}-\frac{e^2}{8\pi\varepsilon_o\left(a+c'\right)^3}}{0.5m_p}} \quad (14.291)$$

From the energy relationship given by Eq. (14.291) and the relationship between the axes given by Eqs. (14.192-14.193) and (14.62-14.63), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (14.291) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=6.0400a_0=3.1962\ X\ 10^{-10}\ m \quad (14.292)$$

Substitution of Eq. (14.292) into Eq. (14.288) gives

$$c'=1.7378a_0=9.1961\ X\ 10^{-11}\ m \quad (14.293)$$

The internuclear distance given by multiplying Eq. (14.293) by two is

$$2c' = 3.4756a_0 = 1.8392\,X\,10^{-10}\ m \tag{14.294}$$

Substitution of Eqs. (14.292-14.293) into Eq. (14.62) gives

$$b = c = 5.7846a_0 = 3.0611\,X\,10^{-10}\ m \tag{14.295}$$

Substitution of Eqs. (14.292-14.293) into Eq. (14.63) gives

$$e = 0.2877 \tag{14.296}$$

From, $2c'_{H-H}$ (Eq. (14.294)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (14.291)), and $2c'_{C-H}$ (Eq. (14.275)), the internuclear distance of each $C-H$ bond, the corresponding bond angle can be determined from the law of cosines. Using, Eq. (13.242), the bond angle θ_{HCH} between the $C-H$ bonds is

$$\theta_{HCH} = \cos^{-1}\left(\frac{2(2.04578)^2-(3.4756)^2}{2(2.04578)^2}\right) = \cos^{-1}(-0.44318) = 116.31^\circ \tag{14.297}$$

The experimental angle between the $C-H$ bonds is [11]

$$\theta_{HCH} = 116.6^\circ \tag{14.298}$$

The $C=C$ bond is along the z-axis. Thus, based on the symmetry of the equivalent bonds, the bond angle $\theta_{C=C-H}$ between the internuclear axis of the $C=C$ bond and a H atom of the CH_2 groups is given by

$$\theta_{C=C-H} = \frac{(360^\circ-\theta_{CHC})}{2} \tag{14.299}$$

Substitution of Eq. (14.298) into Eq. (14.299) gives

$$\theta_{C+C-H} = 121.85^\circ \tag{14.300}$$

The experimental angle between the $C=C-H$ bonds is [11]

$$\theta_{C=C-H} = 121.7^\circ \tag{14.301}$$

and [3]

$$\theta_{C=C-H} = 121.3^\circ \tag{14.302}$$

The $C=C$ bond and H atoms of ethylene line in a plane, and rotation about the $C=C$ is not possible due to conservation of angular momentum in the two sets of spin-paired electrons of the double bond. The CH_2CH_2 MO shown in Figure 42 was rendered using these parameters.

The charge-density in the $C=C$-bond MO is increased by a factor of 0.25 per bond with the formation of the $C_{ethylene}2sp^3$ HOs each having a smaller radius. Using the orbital

composition of the CH_2 groups (Eq. (14.269)) and the $C=C$-bond MO (Eq. (14.242), the radii of $C1s=0.17113a_0$ (Eq. (10.51)) and $C_{ethylene}2sp^3=0.85252a_0$ (Eq. (14.244)) shells, and the parameters of the $C=C$-bond (Eqs. (13.3-13.4), (14.254-14.256), and (14.258-14.268)), the parameters of the $C-H$-bond MOs (Eqs. (13.3-13.4), (14.273-14.275), and (14.277-14.287)), and the bond-angle parameters (Eqs. (14.297-14.302)), the charge-density of the CH_2CH_2 MO comprising the linear combination of two sets of two $C-H$-bond MOs and a $C=C$-bond MO bridging the two CH_2 groups is shown in Figure 42. Each $C-H$-bond MO comprises a H_2-type ellipsoidal MO and a $C_{ethylene}2sp^3$ HO having the dimensional diagram shown in Figure 41. The $C=C$-bond MO comprises a H_2-type ellipsoidal MO bridging two $C_{ethylene}2sp^3$ HOs having the dimensional diagram shown in Figure 40.

ENERGIES OF THE CH_2 GROUPS

The energies of each CH_2 group of ethylene are given by the substitution of the semiprincipal axes (Eqs. (14.273-14.274) and (14.277)) into the energy equations of dihydrogen carbide (Eqs. (13.510-13.514)), with the exception that two times $E_T\left(C=C,2sp^3\right)$ (Eq. (14.247)) is subtracted from $E_T\left(CH_2\right)$ in Eq. (13.514):

$$V_e=2(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-76.00757\ eV \tag{14.303}$$

$$V_p=\frac{2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=26.60266\ eV \tag{14.304}$$

$$T=2(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=24.21459\ eV \tag{14.305}$$

$$V_m=2(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-12.10730\ eV \tag{14.306}$$

$$E_{T_{ethylene}}\left(CH_2\right)=\begin{pmatrix}-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-(-2.26758\ eV)\end{pmatrix}=-49.66493\ eV$$

(14.307)

where $E_{T_{ethylene}}(CH_2)$ is given by Eq. (14.270) which is reiteratively matched to Eq. (13.496) within five-significant-figure round off error.

VIBRATION OF THE $^{12}CH_2$ GROUPS

The vibrational energy levels of CH_2 in ethylene may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $^{12}CH_2$ GROUPS

The equations of the radiation reaction force of the CH_2 groups in ethylene are the same as those of the dihydrogen carbide radical with the substitution of the CH_2-group parameters. Using Eq. (13.515), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.75685\ X\ 10^{16}\ rad/s \tag{14.308}$$

where b is given by Eq. (14.277). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.75685\ X\ 10^{16}\ rad/s = 18.14605\ eV \tag{14.309}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.309) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(18.14605\ eV)}{m_e c^2}} = -0.26660\ eV \tag{14.310}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH_2 due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding

energies, $\overline{E}_D$ given by Eq. (14.310) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having two independent bonds, $\overline{E}'_{ethylene\ osc}\left({}^{12}CH_2\right)$ per bond is

$$\overline{E}'_{ethylene\ osc}\left({}^{12}CH_2\right)=\overline{E}_D+\overline{E}_{Kvib}=\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.311}$$

$$\overline{E}'_{ethylene\ osc}\left({}^{12}CH_2\right)=-0.26660\ eV+\frac{1}{2}(0.35532\ eV)=-0.08894\ eV \tag{14.312}$$

Given that the vibration and reentrant oscillation is for two $C-H$ bonds, $\overline{E}_{ethylene\ osc}\left({}^{12}CH_2\right)$, is:

$$\begin{aligned}\overline{E}_{ethylene\ osc}\left({}^{12}CH_2\right)&=2\left(\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\&=2\left(-0.26660\ eV+\frac{1}{2}(0.35532\ eV)\right)\\&=-0.17788\ eV\end{aligned} \tag{14.313}$$

TOTAL AND DIFFERENCE ENERGIES OF THE ${}^{12}CH_2$ GROUPS

$E_{ethyleneT+osc}\left({}^{12}CH_2\right)$, the total energy of each ${}^{12}CH_2$ group including the Doppler term, is given by the sum of $E_{T_{ethylene}}(CH_2)$ (Eq. (14.307)) and $\overline{E}_{ethylene\ osc}\left({}^{12}CH_2\right)$ given by Eq. (14.313):

$$\begin{aligned}E_{ethyleneT+osc}(CH_2)&=\begin{pmatrix}V_e+T+V_m+V_p+E\left(C,2sp^3\right)\\-2E_T\left(C=C,2sp^3\right)+\overline{E}_{ethylene\ osc}\left({}^{12}CH_2\right)\end{pmatrix}\\&=E_{T_{ethylene}}(CH_2)+\overline{E}_{ethylene\ osc}\left({}^{12}CH_2\right)\end{aligned} \tag{14.314}$$

$$\begin{aligned}E_{ethyleneT+osc}\left({}^{12}CH_2\right)=&\left\{\begin{pmatrix}\frac{-2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-(-2.26759\ eV)\end{pmatrix}\right.\\&\left.-2\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}}{m_e c^2}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\}\\=&-49.66493\ eV-2\left(0.26660\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{14.315}$$

From Eqs. (14.313-14.315), the total energy of each $^{12}CH_2$ is

$$\begin{aligned} E_{ethyleneT+osc}\left(^{12}CH_2\right) &= -49.66493\ eV + \overline{E}_{ethylene\ osc}\left(^{12}CH_2\right) \\ &= -49.66493\ eV - 2\left(0.26660\ eV - \frac{1}{2}(0.35532\ eV)\right) \\ &= -49.84282\ eV \end{aligned} \tag{14.316}$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The total energy for each dihydrogen carbide radical given by Eq. (13.523) is

$$\begin{aligned} E_{radicalT+osc}\left(^{12}CH_2\right) &= -49.66493\ eV + \overline{E}_{radicalosc}\left(^{12}CH_2\right) \\ &= -49.66493\ eV - 2\left(0.25493\ eV - \frac{1}{2}(0.35532\ eV)\right) \\ &= -49.81948\ eV \end{aligned} \tag{14.317}$$

The difference in energy between the CH_2 groups and the dihydrogen carbide radical $\Delta E_{T+osc}\left(^{12}CH_2\right)$ is given by two times the difference between Eqs. (14.316) and (14.317):

$$\begin{aligned} \Delta E_{T+osc}\left(^{12}CH_2\right) &= 2\left(E_{ethyleneT+osc}\left(^{12}CH_2\right) - E_{radicalT+osc}\left(^{12}CH_2\right)\right) \\ &= 2\left(-49.84282\ eV - \left(-49.81948\ eV\right)\right) \\ &= -0.04667\ eV \end{aligned} \tag{14.318}$$

SUM OF THE ENERGIES OF THE $C=C$ σ MO AND THE HOs OF ETHYLENE

The energy components of V_e, V_p, T, V_m, and E_T of the $C=C$-bond MO are the same as those of the CH MO except that each term is multiplied by two corresponding to the double bond and the energy term corresponding to the $C_{ethylene}2sp^3$ HOs in the equation for E_T is zero. The energies of each $C=C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.254-14.255) and (14.258)) into two times the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that zero replaces $E\left(C,2sp^3\right)$ in Eq. (13.453):

$$V_e = 2(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -102.08992\ eV \tag{14.319}$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 21.48386\ eV \tag{14.320}$$

$$T = 2(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 34.67062\ eV \tag{14.321}$$

$$V_m = 2(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -17.33531\ eV \tag{14.322}$$

$$E_T(C=C,\sigma) = -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] = -63.27075\ eV \tag{14.323}$$

where $E_T(C=C,\sigma)$ is the total energy of the $C=C$ σ MO given by Eq. (14.251) which is reiteratively matched to two times Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C=C$-bond MO, $E_T(C=C)$, is given by the sum of two times $E_T(C=C,2sp^3)$, the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of the $C=C$-bond MO (Eq. (14.247)), and $E_T(C=C,\sigma)$, the σ MO contribution given by Eq. (14.252):

$$\begin{aligned} E_T(C=C) &= 2E_T(C=C,2sp^3)+E_T(C=C,\sigma) \\ &= \left(\begin{array}{l} 2(-1.13380\ eV)+ \\ \left(-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\right) \end{array}\right) \\ &= 2(-1.13380\ eV)+(-63.27074\ eV) \\ &= -65.53833\ eV \end{aligned} \tag{14.324}$$

VIBRATION OF ETHYLENE

The vibrational energy levels of CH_2CH_2 may be solved as two sets of two equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $C=C$-BOND MO OF ETHYLENE

The equations of the radiation reaction force of the $C=C$-bond MO are given by Eq. (13.142), except the force-constant factor is $(0.93172)0.5$ based on the force constant k' of

Eq. (14.248), and the $C=C$ -bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega=\sqrt{\frac{0.91771\frac{(0.5)e^2}{4\pi\varepsilon_0 b^3}}{m_e}}=4.30680\,X\,10^{16}\ rad/s \tag{14.325}$$

where b is given by Eq. (14.258). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K=\hbar\omega=\hbar 4.30680\,X\,10^{16}\ rad/s=28.34813\ eV \tag{14.326}$$

In Eq. (11.181), substitution of $E_T(C=C)/2$ (Eq. (14.324)) for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.326) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the two bonds for the reentrant orbit:

$$\overline{E}_D\cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}}=-32.76916\ eV\sqrt{\frac{2e(28.34813\ eV)}{m_e c^2}}=-0.34517\ eV \tag{14.327}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $C=C$ -bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.327) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C=C$ bond. Using the experimental $C=C$ $E_{vib}(\upsilon_3)$ of 1443.5 cm^{-1} $(0.17897\ eV)$ [12] for $\overline{E}_{Kvib}$ of the transition state having two bonds, $\overline{E}'_{osc}(C=C,\sigma)$ per bond is

$$\overline{E}'_{osc}(C=C,\sigma)=\overline{E}_D+\overline{E}_{Kvib}=\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.328}$$

$$\overline{E}'_{osc}(C=C,\sigma)=-0.34517\ eV+\frac{1}{2}(0.17897\ eV)=-0.25568\ eV \tag{14.329}$$

Given that the vibration and reentrant oscillation is for two $C-C$ bonds of the $C=C$ double bond, $\overline{E}_{ethylene\ osc}(C=C,\sigma)$, is:

$$\overline{E}_{ethylene\ osc}(C=C,\sigma)=2\left(\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)=2\left(-0.34517\ eV+\frac{1}{2}(0.17897\ eV)\right)=-0.51136\ eV \tag{14.330}$$

TOTAL ENERGIES OF THE $C=C$ -BOND MO OF ETHYLENE

$E_{T+osc}(C=C)$, the total energy of the $C=C$ -bond MO including the Doppler term, is given by the sum of $E_T(C=C)$ (Eq. (14.324)) and $\overline{E}_{ethylene\ osc}(C=C,\sigma)$ given by Eq. (14.330):

$$\begin{aligned}E_{T+osc}(C=C) &= V_e+T+V_m+V_p+2E_T\left(C=C,2sp^3\right)+\overline{E}_{ethylene\ osc}(C=C,\sigma)\\ &= E_T(C=C,\sigma)+2E_T\left(C=C,2sp^3\right)+\overline{E}_{ethylene\ osc}(C=C,\sigma)\\ &= E_T(C=C)+\overline{E}_{ethylene\ osc}(C=C,\sigma)\end{aligned} \tag{14.331}$$

$$E_{T+osc}(C=C)=\left\{\begin{array}{l}\left(\frac{-2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+2E_T\left(C=C,2sp^3\right)\right)\\ \left(1+(2)\left(\frac{1}{2}\right)\sqrt{\frac{2\hbar\sqrt{\frac{(0.91771)\frac{1}{2}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}}{m_e c^2}}\right)+2\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\} \tag{14.332}$$

$$=-65.53833\ eV-2\left(0.34517\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

From Eqs. (14.330-14.332), the total energy of the $C=C$ -bond MO is

$$\begin{aligned}E_{T+osc}(C=C) &= -63.27074\ eV+2E_T\left(C=C,2sp^3\right)+\overline{E}_{ethylene\ osc}(C=C,\sigma)\\ &= -63.27074\ eV+2(-1.13380\ eV)-2\left(0.34517\ eV-\frac{1}{2}(0.17897\ eV)\right)\\ &= -66.04969\ eV\end{aligned} \tag{14.333}$$

where the experimental E_{vib} was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

BOND ENERGY OF THE $C=C$ BOND OF ETHYLENE

The dissociation energy of the $C=C$ bond of CH_2CH_2, $E_D\left(H_2C=CH_2\right)$, is given by four times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each CH_2 radical that forms the double $C=C$ bond, minus the sum of $\Delta E_{T+osc}\left({}^{12}CH_2\right)$ (Eq. (14.318)), the energy change going from the dihydrogen carbide radicals to the CH_2 groups of ethylene, and $E_{T+osc}(C=C)$ (Eq. (14.333)). Thus, the dissociation energy of the $C=C$ bond of CH_2CH_2, is

$$E_D(H_2C=CH_2)=4\left(E\left(C,2sp^3\right)\right)-\left(\Delta E_{T+osc}\left({}^{12}CH_2\right)+E_{T+osc}(C=C)\right)$$
$$=4(-14.63489\ eV)-(-0.04667\ eV-66.04969\ eV)$$
$$=4(-14.63489\ eV)-(-66.09636\ eV)$$
$$=7.55681\ eV \qquad (14.334)$$

The experimental dissociation energy of the $C=C$ bond of CH_2CH_2 is [7]

$$E_D(H_2C-CH_2)=7.5969\ eV \qquad (14.335)$$

The results of the determination of bond parameters of CH_2CH_2 are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

ACETYLENE MOLECULE ($CHCH$)

The acetylene molecule $CHCH$ is formed by the reaction of two hydrogen carbide radicals:

$$CH+CH\rightarrow CHCH \qquad (14.336)$$

$CHCH$ can be solved using the same principles as those used to solve the methane series $CH_{n=1,2,3,4}$ as well as ethane, wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. First, two sets of one H atomic orbital (AO) combine with two sets of one carbon $2sp^3$ HO to form two hydrogen carbide groups comprising a linear combination of two diatomic H_2-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. Then, the two CH groups bond by forming a H_2-type MO between the remaining three $C2sp^3$ HOs on each carbon atom.

FORCE BALANCE OF THE $C\equiv C$-BOND MO OF ACETYLENE

$CHCH$ comprises a chemical bond between two CH radicals wherein each radical comprises a chemical bond between a carbon and a hydrogen atom. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. The $C-H$ bond of CH having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% H_2-type

ellipsoidal MO and 25% $C2sp^3$ HO. The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H_2, the $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, the MO surface comprises a prolate spheroid at the H proton that is continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of the $C-H$ bond is provided by the spin-pairing force of the CH MO that has the symmetry of an s orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged.

Two CH radicals bond to form $CHCH$ by forming a MO between the two pairs of three remaining $C2sp^3$-HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between two $C2sp^3$ HOs to form a MO comprising six spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy.

As in the case of the $C-H$ bonds, the $C\equiv C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each C atom. The energy of the H_2-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of OH, NH, CH, the $C=O$-bond MO of CO_2, the $C-C$-bond MO of CH_3CH_3, and the $C=C$-bond MO of CH_2CH_2, the $C\equiv C$-bond MO of acetylene must comprise 75% of a H_2-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C\equiv C$-bond MO must comprise a linear combination of three MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$3\left(2C2sp^3+0.75\ H_2\ MO\right)\rightarrow C\equiv C-bond\ MO \tag{14.337}$$

The linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C \equiv C$-bond MO to achieve an energy minimum. The force balance of the $C \equiv C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.337) and the energy matching condition between the $C2sp^3$-HO components of the MO.

Similarly, the energies of each CH MO involve each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the H_2-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. This energy is determined by the considering the effect of the donation of 25% electron density from the three pairs of $C2sp^3$ HOs to the $C \equiv C$-bond MO with the formation of the $C_{acetylene}2sp^3$ HOs each having a smaller radius. The $2sp^3$ hybridized orbital arrangement is given by Eq. (14.140). The sum $E_T\left(C,2sp^3\right)$ of calculated energies of C, C^+, C^{2+}, and C^{3+} is given by Eq. (14.141). The radius r_{2sp^3} of the $C2sp^3$ shell is given by Eq. (14.142). The Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ and the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell are given by Eqs. (14.143) and (14.146), respectively.

Next, consider the formation of the $C \equiv C$-bond MO of acetylene from two CH radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146). The total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C_{acetylene},2sp^3\right)$ of calculated energies of $C2sp^3$, C^+, C^{2+}, and C^{3+} from Eqs. (10.123), (10.113-10.114), (10.68), and (10.48), respectively, is

$$\begin{aligned} E_T\left(C_{acetylene},2sp^3\right) &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + E\left(C,2sp^3\right)\right) \\ &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 14.63489\ eV\right) \\ &= -151.61569\ eV \end{aligned} \tag{14.338}$$

where $E\left(C,2sp^3\right)$ (Eq. (14.146)) is the sum of the energy of C, $-11.27671\ eV$, and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the $E_T\left(C_{acetylene},2sp^3\right)$ is purely Coulombic.

The sharing of electrons between three pairs of $C2sp^3$ HOs to form a $C \equiv C$ -bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating $C2sp^3$ HO donates an excess of 25% of its electron density to the $C \equiv C$ -bond MO to form an energy minimum. By considering this electron redistribution in the acetylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{acetylene2sp^3}$ of the $C2sp^3$ shell of acetylene may be calculated from the Coulombic energy using Eq. (10.102):

$$\begin{aligned} r_{acetylene2sp^3} &= \left(\sum_{n=2}^{5}(Z-n)-0.75\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} \\ &= \frac{9.25e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} \\ &= 0.83008a_0 \end{aligned} \tag{14.339}$$

where $Z=6$ for carbon. Using Eqs. (10.102) and (14.339), the Coulombic energy $E_{Coulomb}\left(C_{acetylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E_{Coulomb}\left(C_{acetylene}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{acetylene2sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.83008a_0} = -16.39089\ eV \tag{14.340}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (13.152). Using Eqs. (14.145) and (14.340), the energy $E\left(C_{acetylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E\left(C_{acetylene}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{acetylene2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = -16.39089\ eV + 0.19086\ eV = -16.20002\ eV \tag{14.341}$$

Thus, $E_T\left(C \equiv C, 2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C \equiv C$ -bond MO is given by the difference between Eq. (14.146) and Eq. (14.341):

$$\begin{aligned} E_T\left(C \equiv C, 2sp^3\right) &= E\left(C_{acetylene}, 2sp^3\right) - E\left(C, 2sp^3\right) \\ &= -16.20002\ eV - \left(-14.63489\ eV\right) \\ &= -1.56513\ eV \end{aligned} \tag{14.342}$$

As in the case of Cl_2, each H_2-type ellipsoidal MO comprises 75% of the $C \equiv C$-bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to each bond of the $C \equiv C$-bond MO causes the electron charge density in Eq. (11.65) to be is given by $\frac{-e}{2} = -0.5e$. The corresponding force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci (Eq. (11.65)) is given by Eq. (14.152). The distance from the origin to each focus c' is given by Eq. (14.153). The internuclear distance is given by Eq. (14.154). The length of the semiminor axis of the prolate spheroidal $C \equiv C$-bond MO $b = c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C \equiv C$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C \equiv C$-bond MO are solved.

The general equations for the energy components of V_e, V_p, T, V_m, and E_T of the $C \equiv C$-bond MO are the same as those of the CH MO except that energy of the $C_{acetylene}2sp^3$ HO is used and the triple-bond nature is considered. In the case of a single bond, the prolate spheroidal H_2-type MO transitions to the $C_{acetylene}2sp^3$ HO of each carbon, and the energy of the $C_{acetylene}2sp^3$ shell must remain constant and equal to the $E\left(C_{acetylene}, 2sp^3\right)$ given by Eq. (14.391). Thus, the energy $E\left(C_{acetylene}, 2sp^3\right)$ in Eq. (14.391) adds to that of the energies of the corresponding H_2-type ellipsoidal MO. The second and third bonds of the triple $C \equiv C$-bond MO also transition to each $C_{acetylene}2sp^3$ HO of each C. The energy of a second and a third H_2-type ellipsoidal MO adds to the first energy component, and the three bonds achieve an energy minimum as a linear combination of the three H_2-type ellipsoidal MOs each having the carbon nuclei as the foci. Each $C-C$-bond MO comprises the same $C_{acetylene}2sp^3$ HO shells of constant energy given by Eq. (14.391). As in the case of the water, NH_2, ammonia, and ethylene molecules given by Eqs. (13.180), (13.320), (13.372), and (14.251), respectively, the energy of the redundant shell is subtracted from the total energy of the linear combination of the σ MO. Thus, the total energy $E_T\left(C \equiv C, \sigma\right)$ of the σ component of the $C \equiv C$-bond MO is given by the sum of the energies of the three bonds each comprising the

linear combination of the $C_{acetylene}2sp^3$ HO and the H_2-type ellipsoidal MO as given by Eq. (14.337) wherein the E_T terms add positively and the $E\left(C_{acetylene},2sp^3\right)$ term is positive due to the sum over a negative and two positive terms. Using Eqs. (13.431) and (14.341), $E_T\left(C\equiv C,\sigma\right)$ is given by

$$\begin{aligned}E_T\left(C\equiv C,\sigma\right) &= E_T + E\left(C_{acetylene},2sp^3\right) - E\left(C_{acetylene},2sp^3\right) - E\left(C_{acetylene},2sp^3\right)\\ &= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] - E\left(C_{acetylene},2sp^3\right)\\ &= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + 16.20002\ eV\end{aligned}$$

(14.343)

The total energy term of the double $C\equiv C$-bond MO is given by the sum of the three H_2-type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition, $E_T\left(C\equiv C,\sigma\right)$ given by Eq. (14.343) is set equal to three times Eq. (13.75):

$$E_T\left(C\equiv C,\sigma\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + 16.20002\ eV = -94.90610\ eV \tag{14.344}$$

From the energy relationship given by Eq. (14.344) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the $C\equiv C$-bond MO can be solved.

Substitution of Eq. (14.153) into Eq. (14.344) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right] = e111.10613 \tag{14.345}$$

The most convenient way to solve Eq. (14.345) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.28714a_0 = 6.81122\ X\ 10^{-11}\ m \tag{14.346}$$

Substitution of Eq. (14.346) into Eq. (14.153) gives

$$c' = 1.13452a_0 = 6.00362\ X\ 10^{-11}\ m \tag{14.347}$$

The internuclear distance given by multiplying Eq. (14.347) by two is

$$2c' = 2.26904a_0 = 1.20072\ X\ 10^{-10}\ m \tag{14.348}$$

The experimental bond distance is [3]

$$2c' = 1.203\ X\ 10^{-10}\ m \tag{14.349}$$

Substitution of Eqs. (14.346-14.347) into Eq. (13.62) gives

$$b = c = 0.60793a_0 = 3.21704\,X\,10^{-11}\ m \tag{14.350}$$

Substitution of Eqs. (14.346-14.347) into Eq. (13.63) gives

$$e = 0.88143 \tag{14.351}$$

The nucleus of the C atoms comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{acetylene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{acetylene2sp^3} = 0.83008a_0$ is the radius of the $C_{acetylene}2sp^3$ shell. Substitution of Eqs. (14.346-14.347) into Eq. (13.261) gives

$$\theta' = 137.91° \tag{14.352}$$

Then, the angle $\theta_{C\equiv C_{acetylene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C\equiv C_{acetylene}2sp^3HO} = 180° - 137.91° = 42.09° \tag{14.353}$$

as shown in Figure 43.

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C\equiv C_{acetylene},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with each $C_{acetylene}2sp^3$ radial vector obeys the following relationship:

$$r_{acetylene2sp^3}\sin\theta_{C\equiv C_{acetylene}2sp^3HO} = 0.83008a_0\sin\theta_{C\equiv C_{acetylene}2sp^3HO} = b\sin\theta_{C\equiv C_{acetylene},H_2MO} \tag{14.354}$$

such that

$$\theta_{C\equiv C_{acetylene},H_2MO} = \sin^{-1}\frac{0.83008a_0\sin\theta_{C\equiv C_{acetylene}2sp^3HO}}{b} = \sin^{-1}\frac{0.83008a_0\sin 42.09°}{b} \tag{14.355}$$

with the use of Eq. (14.353). Substitution of Eq. (14.350) into Eq. (14.355) gives

$$\theta_{C\equiv C_{acetylene},H_2MO} = 66.24° \tag{14.356}$$

Then, the distance $d_{C\equiv C_{acetylene},H_2MO}$ along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C\equiv C_{acetylene},H_2MO} = a\cos\theta_{C\equiv C_{acetylene},H_2MO} \tag{14.357}$$

Substitution of Eqs. (14.346) and (14.356) into Eq. (14.357) gives

$$d_{C\equiv C_{acetylene},H_2MO} = 0.51853a_0 = 2.74396\,X\,10^{-11}\ m \tag{14.358}$$

The distance $d_{C\equiv C_{acetylene}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C\equiv C_{acetylene}2sp^3HO} = c' - d_{C\equiv C_{acetylene},H_2MO} \tag{14.359}$$

Substitution of Eqs. (14.347) and (14.358) into Eq. (14.359) gives

$$d_{C\equiv C_{acetylene}2sp^3HO} = 0.61599a_0 = 3.25966\,X\,10^{-11}\ m \tag{14.360}$$

FORCE BALANCE OF THE CH MOs OF ACETYLENE

The $C-H$ bond of each of the two equivalent CH MOs must comprise 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.429):

$$1\,C2sp^3 + 0.75\,H_2\ MO \rightarrow CH\ MO \tag{14.361}$$

The force balance of the CH MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (13.429) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the CH MO are solved.

Consider the formation of the triple $C\equiv C$-bond MO of acetylene from two CH radicals, each having a $C2sp^3$ shell with an energy given by Eq. (14.146). The energy components of V_e, V_p, T, V_m, and E_T are the same as those of the hydrogen carbide radical, except that two times $E_T\left(C\equiv C,2sp^3\right)$ is subtracted from $E_T\left(CH\right)$ of Eq. (13.495). The subtraction of the energy change of the $C2sp^3$ shells with the formation of the $C\equiv C$-bond

MO matches the energy of the $C-H$-bond MOs to the decrease in the energy of the $C2sp^3$ HOs. Using Eqs. (13.495) and (14.342), $E_{T_{acetylene}}(CH)$ is given by

$$E_{T_{acetylene}}(CH) = E_T + E\left(C,2sp^3\right) - 2E_T\left(C \equiv C,2sp^3\right)$$
$$= \begin{pmatrix} -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV-(-3.13026\ eV) \end{pmatrix} \quad (14.362)$$

$E_{T_{acetylene}}(CH)$ given by Eq. (14.362) is set equal to the energy of the H_2-type ellipsoidal MO given by Eq. (13.75):

$$E_{T_{acetylene}}(CH) = \begin{pmatrix} -\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \\ -14.63489\ eV-(-3.13026\ eV) \end{pmatrix} = -31.63537\ eV \quad (14.363)$$

From the energy relationship given by Eq. (14.363) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.363) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e20.13074 \quad (14.364)$$

The most convenient way to solve Eq. (14.364) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.48719a_0 = 7.86987\,X\,10^{-11}\ m \quad (14.365)$$

Substitution of Eq. (14.365) into Eq. (14.60) gives

$$c' = 0.99572a_0 = 5.26913\,X\,10^{-11}\ m \quad (14.366)$$

The internuclear distance given by multiplying Eq. (14.366) by two is

$$2c' = 1.99144a_0 = 1.05383\,X\,10^{-10}\ m \quad (14.367)$$

The experimental bond distance is [3]

$$2c' = 1.060\,X\,10^{-10}\ m \quad (14.368)$$

Substitution of Eqs. (14.365-14.366) into Eq. (14.62) gives

$$b = c = 1.10466a_0 = 5.84561\,X\,10^{-11}\ m \quad (14.369)$$

Substitution of Eqs. (14.365-14.366) into Eq. (14.63) gives

$$e = 0.66953 \quad (14.370)$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{acetylene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{acetylene2sp^3} = 0.83008a_0$ is the radius of the $C_{acetylene}2sp^3$ shell. Substitution of Eqs. (14.365-14.366) into Eq. (13.261) gives

$$\theta' = 90.99° \tag{14.371}$$

Then, the angle $\theta_{C-H_{acetylene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-H_{acetylene}2sp^3HO} = 180° - 90.99° = 89.01° \tag{14.372}$$

as shown in Figure 43. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C-H_{acetylene},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C_{acetylene}2sp^3$ radial vector obeys the following relationship:

$$r_{acetylene2sp^3}\sin\theta_{C-H_{acetylene}2sp^3HO} = 0.83008a_0\sin\theta_{C-H_{acetylene}2sp^3HO} = b\sin\theta_{C-H_{acetylene},H_2MO} \tag{14.373}$$

such that

$$\theta_{C-H_{acetylene},H_2MO} = \sin^{-1}\frac{0.83008a_0\sin\theta_{C-H_{acetylene}2sp^3HO}}{b} = \sin^{-1}\frac{0.83008a_0\sin 89.01°}{b} \tag{14.374}$$

with the use of Eq. (14.372). Substitution of Eq. (14.369) into Eq. (14.374) gives

$$\theta_{C-H_{acetylene},H_2MO} = 48.71° \tag{14.375}$$

Then, the distance $d_{C-H_{acetylene},H_2MO}$ along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{acetylene},H_2MO} = a\cos\theta_{C-H_{acetylene},H_2MO} \tag{14.376}$$

Substitution of Eqs. (14.365) and (14.375) into Eq. (14.376) gives

$$d_{C-H_{acetylene},H_2MO} = 0.98145a_0 = 5.19359\,X\,10^{-11}\ m \tag{14.377}$$

The distance $d_{C-H_{acetylene}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{acetylene}2sp^3HO} = c' - d_{C-H_{acetylene},H_2MO} \tag{14.378}$$

Substitution of Eqs. (14.366) and (14.377) into Eq. (14.378) gives

$$d_{C-H_{acetylene}2sp^3HO} = 0.01427a_0 = 7.55329\,X\,10^{-13}\ m \tag{14.379}$$

With the $C \equiv C$ double bond along one axis, the minimum energy is obtained with the $C-H$-bond MO at a maximum separation. Thus, the bond angle $\theta_{C\equiv C-H}$ between the internuclear axis of the $C \equiv C$ bond and the H atom of the CH groups is

$$\theta_{C\equiv C-H} = 180° \tag{14.380}$$

The experimental angle between the $C \equiv C-H$ bonds is [6]

$$\theta_{C\equiv C-H} = 180° \tag{14.381}$$

The $CHCH$ MO shown in Figure 44 was rendered using these parameters.

The charge-density in the $C \equiv C$-bond MO is increased by a factor of 0.25 per bond with the formation of the $C_{acetylene}2sp^3$ HOs each having a smaller radius. Using the orbital composition of the CH groups (Eq. (14.361)) and the $C \equiv C$-bond MO (Eq. (14.337), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)) and $C_{acetylene}2sp^3 = 0.83008a_0$ (Eq. (14.339)) shells, and the parameters of the $C \equiv C$-bond (Eqs. (13.3-13.4), (14.346-14.348), and (14.350-14.360)), the parameters of the $C-H$-bond MOs (Eqs. (13.3-13.4), (14.365-14.367), and (14.369-14.379)), and the bond-angle parameter (Eqs. (14.380-14.381)), the charge-density of the $CHCH$ MO comprising the linear combination of two $C-H$-bond MOs and a $C \equiv C$-bond MO bridging the two CH groups is shown in Figure 44. Each $C-H$-bond MO comprises a H_2-type ellipsoidal MO and a $C_{acetylene}2sp^3$ HO having the dimensional diagram shown in Figure 43. The $C \equiv C$-bond MO comprises a H_2-type ellipsoidal MO bridging two $C_{acetylene}2sp^3$ HOs having the dimensional diagram also shown in Figure 43.

ENERGIES OF THE CH GROUPS

The energies of each CH group of acetylene are given by the substitution of the semiprincipal axes (Eqs. (14.365-14.366) and (14.369)) into the energy equations of hydrogen carbide (Eqs. (13.510-13.514)), with the exception that two times $E_T\left(C \equiv C, 2sp^3\right)$ (Eq. (14.342)) is subtracted from $E_T\left(CH\right)$ in Eq. (13.514):

$$V_e = \left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -40.62396\ eV \tag{14.382}$$

$$V_p = \frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 13.66428\ eV \tag{14.383}$$

$$T=(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=13.65796\ eV \tag{14.384}$$

$$V_m=(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-6.82898\ eV \tag{14.385}$$

$$E_{T_{acetylene}}(CH)=\begin{pmatrix}-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-(-3.13026\ eV)\end{pmatrix}=-31.63532\ eV$$

(14.386)

where $E_{T_{acetylene}}(CH)$ is given by Eq. (14.362) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

VIBRATION OF THE ^{12}CH GROUPS

The vibrational energy levels of CH in acetylene may be solved using the methods given in the Vibration and Rotation of CH section.

THE DOPPLER ENERGY TERMS OF THE ^{12}CH GROUPS

The equations of the radiation reaction force of the CH groups in acetylene are the same as those of the hydrogen carbide radical with the substitution of the CH-group parameters. Using Eq. (13.477), the angular frequency of the reentrant oscillation in the transition state is

$$\omega=\sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}}=3.08370\,X\,10^{16}\ rad/s \tag{14.387}$$

where b is given by Eq. (14.369). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K=\hbar\omega=\hbar 3.08370\,X\,10^{16}\ rad/s=20.29747\ eV \tag{14.388}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.388) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D\cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}}=-31.63537\ eV\sqrt{\frac{2e(20.29747\ eV)}{m_e c^2}}=-0.28197\ eV \tag{14.389}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.389) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state, $\overline{E}_{acetylene\ osc}\left({}^{12}CH\right)$ is

$$\overline{E}_{acetylene\ osc}\left({}^{12}CH\right)=\overline{E}_D+\overline{E}_{Kvib}=\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.390}$$

$$\overline{E}_{acetylene\ osc}\left({}^{12}CH\right)=-0.28197\ eV+\frac{1}{2}(0.35532\ eV)=-0.10430\ eV \tag{14.391}$$

TOTAL AND DIFFERENCE ENERGIES OF THE ${}^{12}CH$ GROUPS

$E_{acetyleneT+osc}\left({}^{12}CH\right)$, the total energy of each ${}^{12}CH$ group including the Doppler term, is given by the sum of $E_{T_{acetylene}}(CH)$ (Eq. (14.386)) and $\overline{E}_{acetylene\ osc}\left({}^{12}CH\right)$ given by Eq. (14.391):

$$\begin{aligned}E_{acetyleneT+osc}(CH)&=\begin{pmatrix}V_e+T+V_m+V_p+E\left(C,2sp^3\right)\\-2E_T\left(C\equiv C,2sp^3\right)+\overline{E}_{acetylene\ osc}\left({}^{12}CH\right)\end{pmatrix}\\&=E_{T_{acetylene}}(CH)+\overline{E}_{acetylene\ osc}\left({}^{12}CH\right)\end{aligned} \tag{14.392}$$

$$\begin{aligned}E_{acetyleneT+osc}\left({}^{12}CH\right)&=\left\{\begin{pmatrix}\frac{-e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-(-3.13026\ eV)\end{pmatrix}\right.\\&\left.-\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}\frac{m_e}{m_e}}{m_e c^2}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\}\\&=-31.63537\ eV-\left(0.28197\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{14.393}$$

From Eqs. (14.391-14.393), the total energy of each ${}^{12}CH$ is

$$E_{acetyleneT+osc}\left({}^{12}CH\right)=-31.63537\ eV+\bar{E}_{acetylene\ osc}\left({}^{12}CH\right)$$
$$=-31.63537\ eV-\left(0.28197\ eV-\frac{1}{2}(0.35532\ eV)\right) \quad (14.394)$$
$$=-31.73967\ eV$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The total energy for each hydrogen carbide radical given by Eq. (13.485) is

$$E_{radicalT+osc}\left({}^{12}CH\right)=-31.63537\ eV+\bar{E}_{radicalosc}\left({}^{12}CH\right)$$
$$=-31.63537\ eV-0.24966\ eV+\frac{1}{2}(0.35532\ eV) \quad (14.395)$$
$$=-31.70737\ eV$$

The difference in energy between the CH groups and the hydrogen carbide radical $\Delta E_{T+osc}\left({}^{12}CH\right)$ is given by two times the difference between Eqs. (14.394) and (14.395):

$$\Delta E_{T+osc}\left({}^{12}CH\right)=2\left(E_{acetyleneT+osc}\left({}^{12}CH\right)-E_{radicalT+osc}\left({}^{12}CH\right)\right)$$
$$=2\left(-31.73967\ eV-\left(-31.70737\ eV\right)\right) \quad (14.396)$$
$$=-0.06460\ eV$$

SUM OF THE ENERGIES OF THE $C\equiv C$ σ MO AND THE HOs OF ACETYLENE

The energy components of V_e, V_p, T, V_m, and E_T of the $C\equiv C$-bond MO are the same as those of the CH MO except that each term is multiplied by three corresponding to the triple bond and the energy term corresponding to the $C_{acetylene}2sp^3$ HOs in the equation for E_T is positive. The energies of each $C\equiv C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.346-14.347) and (14.350)) into three times the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that $E\left(C,2sp^3\right)$ in Eq. (13.453) is positive and given by Eq. (14.341):

$$V_e=3\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-182.53826\ eV \quad (14.397)$$

$$V_p=3\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=35.97770\ eV \quad (14.398)$$

$$T = 3(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 70.90876\ eV \tag{14.399}$$

$$V_m = 3(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -35.45438\ eV \tag{14.400}$$

$$E_T(C\equiv C,\sigma) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+16.20002\ eV = -94.90616\ eV \tag{14.401}$$

where $E_T(C\equiv C,\sigma)$ is the total energy of the $C\equiv C$ σ MO given by Eq. (14.343) which is reiteratively matched to three times Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C\equiv C$-bond MO, $E_T(C\equiv C)$, is given by the sum of two times $E_T(C\equiv C,2sp^3)$, the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of the $C\equiv C$-bond MO (Eq. (14.342)), and $E_T(C\equiv C,\sigma)$, the σ MO contribution given by Eq. (14.344):

$$\begin{aligned}E_T(C\equiv C) &= 2E_T(C\equiv C,2sp^3)+E_T(C\equiv C,\sigma)\\ &= \left(\begin{array}{l}2(-1.56513\ eV)+\\ \left(-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+16.20002\ eV\right)\end{array}\right)\\ &= 2(-1.56513\ eV)+(-94.90610\ eV)\\ &= -98.03637\ eV\end{aligned} \tag{14.402}$$

VIBRATION OF ACETYLENE

The vibrational energy levels of $CHCH$ may be solved as two equivalent coupled harmonic oscillators with a bridging harmonic oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $C \equiv C$-BOND MO OF ACETYLENE

The equations of the radiation reaction force of the $C \equiv C$-bond MO are given by Eq. (14.231), except that the $C \equiv C$-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.5e^2}{4\pi\varepsilon_0 a^3}}{m_e}} = 2.00186\,X\,10^{16}\ rad/s \tag{14.403}$$

where a is given by Eq. (14.346). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.00186\,X\,10^{16}\ rad/s = 13.17659\ eV \tag{14.404}$$

In Eq. (11.181), substitution of $E_T(C \equiv C)/3$ (Eq. (14.402)) for E_{hv}, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.404) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -32.67879\ eV\sqrt{\frac{2e(13.17659\ eV)}{m_e c^2}} = -0.23468\ eV \tag{14.405}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $C \equiv C$-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.405) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C \equiv C$ bond. Using the experimental $C \equiv C$ $E_{vib}(\upsilon_3)$ of 3374 cm^{-1} (0.41833 eV) [6] for $\overline{E}_{Kvib}$ of the transition state having three bonds, $\overline{E}'_{osc}(C \equiv C, \sigma)$ per bond is

$$\overline{E}'_{osc}(C \equiv C, \sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.406}$$

$$\overline{E}'_{osc}(C \equiv C, \sigma) = -0.23468\ eV + \frac{1}{2}(0.41833\ eV) = -0.02551\ eV \tag{14.407}$$

Given that the vibration and reentrant oscillation is for three $C-C$ bonds of the $C \equiv C$ triple bond, $\overline{E}_{acetylene\ osc}(C \equiv C, \sigma)$, is:

$$\begin{aligned}\bar{E}_{acetylene\ osc}(C\equiv C,\sigma) &= 3\left(\bar{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 3\left(-0.23468\ eV+\frac{1}{2}(0.41833\ eV)\right)\\ &= -0.07654\ eV\end{aligned} \tag{14.408}$$

TOTAL ENERGIES OF THE $C\equiv C$ -BOND MO OF ACETYLENE

$E_{T+osc}(C\equiv C)$, the total energy of the $C\equiv C$ -bond MO including the Doppler term, is given by the sum of $E_T(C\equiv C)$ (Eq. (14.402)) and $\bar{E}_{acetylene\ osc}(C\equiv C,\sigma)$ given by Eq. (14.408):

$$\begin{aligned}E_{T+osc}(C\equiv C) &= \begin{pmatrix}V_e+T+V_m+V_p-E\left(C_{acetylene},2sp^3\right)\\ +2E_T\left(C\equiv C,2sp^3\right)+\bar{E}_{acetylene\ osc}(C\equiv C,\sigma)\end{pmatrix}\\ &= E_T(C\equiv C,\sigma)+2E_T\left(C\equiv C,2sp^3\right)+\bar{E}_{acetylene\ osc}(C\equiv C,\sigma)\\ &= E_T(C\equiv C)+\bar{E}_{acetylene\ osc}(C\equiv C,\sigma)\end{aligned} \tag{14.409}$$

$$\begin{aligned}E_{T+osc}(C\equiv C) &= \left\{\begin{pmatrix}\frac{-3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\ -E\left(C_{acetylene},2sp^3\right)+2E_T\left(C\equiv C,2sp^3\right)\end{pmatrix}\right\}\\ &\quad\left\{\begin{pmatrix}1+(3)\left(\frac{1}{3}\right)\sqrt{\frac{2\hbar\sqrt{\frac{\frac{1}{2}\frac{e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}}\end{pmatrix}+3\left(\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\}\\ &= -98.03637\ eV-3\left(0.23468\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{14.410}$$

From Eqs. (14.408-14.410), the total energy of the $C\equiv C$ -bond MO is

$$\begin{aligned}E_{T+osc}(C\equiv C) &= -94.90610\ eV+2E_T\left(C\equiv C,2sp^3\right)+\bar{E}_{acetylene\ osc}(C\equiv C,\sigma)\\ &= -94.90610\ eV+2(-1.56513\ eV)-3\left(0.23468\ eV-\frac{1}{2}(0.41833\ eV)\right)\\ &= -98.11291\ eV\end{aligned} \tag{14.411}$$

where the experimental E_{vib} was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

BOND ENERGY OF THE $C \equiv C$ BOND OF ACETYLENE

As in the case of $^{12}CH_2$ and ^{14}NH, the dissociation of the $C \equiv C$ bond forms three unpaired electrons per central atom wherein the magnetic moments cannot all cancel. The energy per atom $E(magnetic)$ is given by Eq. (13.524). Thus, the dissociation energy of the $C \equiv C$ bond of $CHCH$, $E_D(HC \equiv CH)$, is given by six times $E(C, 2sp^3)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each CH radical that forms the triple $C \equiv C$ bond, minus the sum of $\Delta E_{T+osc}(^{12}CH)$ (Eq. (14.396)), the energy change going from the hydrogen carbide radicals to the CH groups of acetylene, $E_{T+osc}(C \equiv C)$ (Eq. (14.411)), and two times $E(magnetic)$ given by Eq. (13.524). Thus, the dissociation energy of the $C \equiv C$ bond of $CHCH$, is

$$\begin{aligned} E_D(HC \equiv CH) &= 6\left(E(C, 2sp^3)\right) - \left(\Delta E_{T+osc}(^{12}CH) + E_{T+osc}(C \equiv C) + 2E(magnetic)\right) \\ &= 6(-14.63489\ eV) - (-0.06460\ eV - 98.11291\ eV + 0.29606\ eV) \\ &= 6(-14.63489\ eV) - (-97.88145\ eV) \\ &= 10.07212\ eV \end{aligned} \tag{14.412}$$

The experimental dissociation energy of the $C \equiv C$ bond of $CHCH$ is [7]

$$E_D(HC \equiv CH) = 10.0014\ eV \tag{14.413}$$

The results of the determination of bond parameters of $CHCH$ are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

BENZENE MOLECULE (C_6H_6)

The benzene molecule C_6H_6 is formed by the reaction of three ethylene molecules:

$$3CH_2CH_2 \rightarrow C_6H_6 + 3H_2 \tag{14.414}$$

C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each $2sp^3$ HO of each carbon atom initially has four unpaired electrons. Thus, the $6H$ atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3-hybridized carbon

atoms contribute twenty-four electrons to form six $C-H$ bonds and six $C=C$ bonds. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. Each $C=C$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ and each $C=C$ bond comprises a linear combination of one and two diatomic H_2-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

FORCE BALANCE OF THE $C=C$-BOND MO OF BENZENE

C_6H_6 can be considered a linear combination of three ethylene molecules wherein a $C-H$ bond of each CH_2 group of $H_2C=CH_2$ is replaced by a $C=C$ bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. Before forming ethylene groups, the $2sp^3$ hybridized orbital arrangement of each carbon atom is given by Eq. (14.140). The sum $E_T\left(C,2sp^3\right)$ of calculated energies of C, C^+, C^{2+}, and C^{3+} is given by Eq. (14.141). The radius r_{2sp^3} of the $C2sp^3$ shell is given by Eq. (14.142). The Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ and the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell are given by Eqs. (14.143) and (14.146), respectively. Two CH_2 radicals bond to form CH_2CH_2 by forming a MO between the two pairs of remaining $C2sp^3$-HO electrons of the two carbon atoms. However, in this case, the sharing of electrons between four $C2sp^3$ HOs to form a MO comprising four spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy. The $C=C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each C atom. The energy of the H_2-type ellipsoidal MO is matched to that of each $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as those of OH, NH, CH, the $C=O$-bond MO of CO_2, and the $C-C$-bond MO of CH_3CH_3, the $C=C$-bond MO of ethylene must comprise 75% of a H_2-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C=C$-bond MO must comprise

a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$2\left(2\,C2sp^3 + 0.75\,H_2\ MO\right) \rightarrow C=C-bond\ MO \tag{14.415}$$

The linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. The force balance of the $C=C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.415) and the energy matching condition between the $C2sp^3$-HO components of the MO.

The sharing of electrons between two pairs of $C2sp^3$ HOs to form a $C=C$-bond MO permits each participating hybridized orbital to decrease in radius and energy. The sum $E_T\left(C_{ethylene}, 2sp^3\right)$ of calculated energies of $C2sp^3$, C^+, C^{2+}, and C^{3+} is given by Eq. (14.243). In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating $C2sp^3$ HO donates an excess of 25% of its electron density to the $C=C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethylene2sp^3}$ of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E\left(C_{ethylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is given by Eq. (14.246). $E_T\left(C=C, 2sp^3\right)$ (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between $E\left(C_{ethylene}, 2sp^3\right)$ and $E\left(C, 2sp^3\right)$.

Consider the case where three sets of $C=C$-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\begin{pmatrix} 3\left(2\ C2sp^3 + 0.75\ H_2\ MO\right) \rightarrow 3\left(C \overset{4e}{=} C\right) - ethylene - type - bond\ MO \\ \rightarrow 6\left(C \overset{3e}{=} C\right) - bond\ MO\ of\ benzene \end{pmatrix} \tag{14.416}$$

The linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond $C=C$-bond are determined using the same equations as those used to determine the same parameters of the $C=C$-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene. The energies of each $C=C$ bond of benzene are also determined using the same equations as those of ethylene with the parameters of benzene. The result is that the energies are essentially given as 0.75 times the energies of the $C=C$-bond MO of ethylene (Eqs. (14.251-14.253) and (14.319-14.333).

The derivation of the dimensional parameters of benzene follows the same procedure as the determination of those of ethylene. As in the case of ethylene, each H_2-type ellipsoidal MO comprises 75% of the $C=C$-bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to each bond of the $C=C$-bond MO causes the electron charge density in Eq. (11.65) to be is given by $\frac{-e}{2} = -0.5e$. The corresponding force constant k' is given by Eq. (14.152). In addition, the energy matching at all six $C2sp^3$ HOs further requires that k' be corrected by a hybridization factor (Eq. (13.430)) as in the case of ethylene, expect that the constraint that the bonds connect a six-member ring of $C=C$ bonds of benzene rather two $C2sp^3$ HOs of ethylene decreases the hybridization factor of benzene compared to that of ethylene (Eq. (14.248)).

Since the energy of each H_2-type ellipsoidal MO is matched to that of all the continuously connected $C_{benzene}2sp^3$ HOs, the hybridization-energy-matching factor is 0.85252. Hybridization with 25% electron donation to each $C=C$-bond gives rise to the $C_{benzene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$ given by Eq. (14.245). The corresponding hybridization factor is given by the ratio of $15.95955\ eV$, the magnitude of

$E_{Coulomb}\left(C_{benzene},2sp^3\right)$ given by Eq. (14.245), and $13.605804\,eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The hybridization energy factor $C_{benzeneC2sp^3HO}$ is

$$C_{benzeneC2sp^3HO}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{benzene2sp^3}}}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.85252a_0}}=\frac{13.605804\,eV}{15.95955\,eV}=0.85252 \quad (14.417)$$

Thus, the force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci (Eq. (11.65)) is given by

$$k'=C_{benzeneC2sp^3HO}\frac{(0.5)2e^2}{4\pi\varepsilon_0}=0.85252\frac{(0.5)2e^2}{4\pi\varepsilon_0} \quad (14.418)$$

The distance from the origin to each focus c' is given by substitution of Eq. (14.418) into Eq. (13.60). Thus, the distance from the origin of the component of the double $C=C$ -bond MO to each focus c' is given by

$$c'=a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{(0.85252)m_e e^2 a}}=\sqrt{\frac{aa_0}{0.85252}} \quad (14.419)$$

The internuclear distance from Eq. (14.419) is

$$2c'=2\sqrt{\frac{aa_0}{0.85252}} \quad (14.420)$$

The length of the semiminor axis of the prolate spheroidal $C=C$ -bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C=C$ -bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C=C$ -bond MO are solved.

The general equations for the energy components of V_e, V_p, T, V_m, and E_T of the $C=C$ -bond MO of benzene are the same as those of the CH_2CH_2 MO except that energy of the $C_{benzene}2sp^3$ HO is used and the hybridization factor is given by Eq. (14.417). Using Eqs. (14.251) and (14.417), $E_T\left(C=C,\sigma\right)$ is given by

$$\begin{aligned}E_T\left(C=C,\sigma\right)&=E_T+E\left(C_{benzene},2sp^3\right)-E\left(C_{benzene},2sp^3\right)\\&=-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\end{aligned} \quad (14.421)$$

The total energy term of the double $C=C$ -bond MO is given by the sum of the two H_2-type ellipsoidal MOs given by Eq. (11.212). To match this boundary condition, $E_T(C=C,\sigma)$ given by Eq. (14.421) is set equal to two times Eq. (13.75):

$$E_T(C=C,\sigma)=-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]=-63.27074\ eV \tag{14.422}$$

From the energy relationship given by Eq. (14.422) and the relationship between the axes given by Eqs. (14.419-14.420) and (13.62-13.63), the dimensions of the $C=C$ -bond MO can be solved.

Substitution of Eq. (14.419) into Eq. (14.422) gives

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{0.85252}}}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{0.85252}}}{a-\sqrt{\frac{aa_0}{0.85252}}}-1\right]=e63.27074 \tag{14.423}$$

The most convenient way to solve Eq. (14.423) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=1.47348a_0=7.79733\ X\ 10^{-11}\ m \tag{14.424}$$

Substitution of Eq. (14.424) into Eq. (14.4129) gives

$$c'=1.31468a_0=6.95699\ X\ 10^{-11}\ m \tag{14.425}$$

The internuclear distance given by multiplying Eq. (14.425) by two is

$$2c'=2.62936a_0=1.39140\ X\ 10^{-10}\ m \tag{14.426}$$

The experimental bond distance is [3]

$$2c'=1.339\ X\ 10^{-10}\ m \tag{14.427}$$

Substitution of Eqs. (14.424-14.425) into Eq. (13.62) gives

$$b=c=0.66540a_0=3.52116\ X\ 10^{-11}\ m \tag{14.428}$$

Substitution of Eqs. (14.424-14.425) into Eq. (13.63) gives

$$e=0.89223 \tag{14.429}$$

The nucleus of the C atoms comprise the foci of the H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{benzene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). Each benzene carbon atom contributes $(0.75)(-1.13380\ eV)=-0.85035\ eV$ (Eqs. (14.483) and (14.493)) to each of the two $C\overset{3e}{=}C$ -bond MOs and $(0.5)(-1.13380\ eV)=-0.56690\ eV$ (Eq. (14.467)) to the corresponding

$C-H$-bond MO. The energy contribution due to the charge donation at each carbon superimposes linearly. The radius of $r_{benzene2sp^3} = 0.79597a_0$ is calculated using Eq. (14.518) using the total energy donation to each bond with which it is participates in bonding. The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{benzene2sp^3} = 0.79597a_0$ is the radius of the $C_{benzene}2sp^3$ shell. Substitution of Eqs. (14.424-14.425) into Eq. (13.261) gives

$$\theta' = 134.24° \tag{14.430}$$

Then, the angle $\theta_{C=C_{benzene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C=C_{benzene}2sp^3HO} = 180° - 134.24° = 45.76° \tag{14.431}$$

as shown in Figure 45.

Thus, the $^{12}CH_4$ bond dissociation energy, $E_D\left(^{12}CH_4\right)$, given by Eqs. (13.154), and (13.614-13.616) is

$$\begin{aligned} E_D\left(^{12}CH_4\right) &= -\left(67.95529\ eV + 13.59844\ eV\right) - E_{T+osc}\left(^{12}CH_4\right) \\ &= -81.55373\ eV - \left(-86.04373\ eV\right) \\ &= 4.4900\ eV \end{aligned} \tag{13.617}$$

The experimental $^{12}CH_4$ bond dissociation energy is [40]

$$E_D\left(^{12}CH_4\right) = 4.48464\ eV \tag{13.618}$$

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C=C_{benzene},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with each $C_{benzene}2sp^3$ radial vector obeys the following relationship:

$$r_{benzene2sp^3}\sin\theta_{C=C_{benzene}2sp^3HO} = 0.79597a_0\sin\theta_{C=C_{benzene}2sp^3HO} = b\sin\theta_{C=C_{benzene},H_2MO} \tag{14.432}$$

such that

$$\theta_{C=C_{benzene},H_2MO} = \sin^{-1}\frac{0.79597a_0\sin\theta_{C=C_{benzene}2sp^3HO}}{b} = \sin^{-1}\frac{0.79597a_0\sin 45.76°}{b} \tag{14.433}$$

with the use of Eq. (14.431). Substitution of Eq. (14.428) into Eq. (14.433) gives

$$\theta_{C=C_{benzene},H_2MO} = 58.98° \tag{14.434}$$

Then, the distance $d_{C=C_{benzene},H_2MO}$ along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C=C_{benzene},H_2MO} = a\cos\theta_{C=C_{benzene},H_2MO} \quad (14.435)$$

Substitution of Eqs. (14.424) and (14.434) into Eq. (14.435) gives

$$d_{C=C_{benzene},H_2MO} = 0.75935a_0 = 4.01829\,X\,10^{-11}\ m \quad (14.436)$$

The distance $d_{C=C_{benzene}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C=C_{benzene}2sp^3HO} = c' - d_{C=C_{benzene},H_2MO} \quad (14.437)$$

Substitution of Eqs. (14.425) and (14.436) into Eq. (14.437) gives

$$d_{C=C_{benzene}2sp^3HO} = 0.55533a_0 = 2.93870\,X\,10^{-11}\ m \quad (14.438)$$

FORCE BALANCE OF THE CH MOs OF BENZENE

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Each $C-H$ bond of CH having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% H_2-type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.439):

$$1\,C2sp^3 + 0.75\,H_2\ MO \rightarrow CH\ MO \quad (14.439)$$

The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H_2, the $C-H$-bond MO is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus.

The force balance of the CH MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.439) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO. The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH MO in terms of the central force of the foci is given by Eq. (13.59). The distance

from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the CH MO are solved.

Consider the formation of the double $C=C$-bond MOs of benzene wherein ethylene formed from two CH_2 radicals, each having a $C2sp^3$ shell with an energy given by Eq. (14.146), serves as a basis element. The energy components of V_e, V_p, T, V_m, and E_T are the same as those of the hydrogen carbide radical, except that $E_T\left(C=C,2sp^3\right)$ is subtracted from $E_T\left(CH\right)$ of Eq. (13.495). As in the case of the CH_2 groups of ethylene (Eq. (14.270)), the subtraction of the energy change of the $C2sp^3$ shell per H with the formation of the $C=C$-bond MO matches the energy of each $C-H$-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. Using Eqs. (13.431) and (14.247), $E_{T_{benzene}}\left(CH\right)$ is given by

$$E_{T_{benzene}}\left(CH\right)=E_T+E\left(C,2sp^3\right)-E_T\left(C=C,2sp^3\right)$$
$$=\begin{pmatrix}-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\ -14.63489\ eV-(-1.13379\ eV)\end{pmatrix} \quad (14.440)$$

$E_{T_{benzene}}\left(CH\right)$ given by Eq. (14.440) is set equal to the energy of the H_2-type ellipsoidal MO given by Eq. (13.75):

$$E_{T_{benzene}}\left(CH\right)=\begin{pmatrix}-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\ -14.63489\ eV-(-1.13379\ eV)\end{pmatrix}=-31.63537\ eV$$

(14.441)

From the energy relationship given by Eq. (14.441) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.441) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right]=e18.13427 \quad (14.442)$$

The most convenient way to solve Eq. (14.442) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.60061a_0 = 8.47006\,X\,10^{-11}\ m \tag{14.443}$$

Substitution of Eq. (14.443) into Eq. (14.60) gives

$$c' = 1.03299a_0 = 5.46636\,X\,10^{-11}\ m \tag{14.444}$$

The internuclear distance given by multiplying Eq. (14.444) by two is

$$2c' = 2.06598a_0 = 1.09327\,X\,10^{-10}\ m \tag{14.445}$$

The experimental bond distance is [3]

$$2c' = 1.101\,X\,10^{-10}\ m \tag{14.446}$$

Substitution of Eqs. (14.443-14.444) into Eq. (14.62) gives

$$b = c = 1.22265a_0 = 6.47000\,X\,10^{-11}\ m \tag{14.447}$$

Substitution of Eqs. (14.443-14.444) into Eq. (14.63) gives

$$e = 0.64537 \tag{14.448}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{benzene}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{benzene2sp^3} = 0.79597a_0$ is the radius of the $C_{benzene}2sp^3$ shell. Substitution of Eqs. (14.443-14.444) into Eq. (13.261) gives

$$\theta' = 74.42° \tag{14.449}$$

Then, the angle $\theta_{C-H_{benzene}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-H_{benzene}2sp^3HO} = 180° - 74.42° = 105.58° \tag{14.450}$$

as shown in Figure 46.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C-H_{benzene},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C_{benzene}2sp^3$ radial vector obeys the following relationship:

$$r_{benzene2sp^3}\sin\theta_{C-H_{benzene}2sp^3HO} = 0.79597a_0\sin\theta_{C-H_{benzene}2sp^3HO} = b\sin\theta_{C-H_{benzene},H_2MO} \tag{14.451}$$

such that

$$\theta_{C-H_{benzene},H_2MO} = \sin^{-1}\frac{0.79597a_0 \sin\theta_{C-H_{benzene}2sp^3HO}}{b} = \sin^{-1}\frac{0.79597a_0 \sin 105.58°}{b} \quad (14.452)$$

with the use of Eq. (14.450). Substitution of Eq. (14.447) into Eq. (14.452) gives

$$\theta_{C-H_{benzene},H_2MO} = 38.84° \quad (14.453)$$

Then, the distance $d_{C-H_{benzene},H_2MO}$ along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{benzene},H_2MO} = a\cos\theta_{C-H_{benzene},H_2MO} \quad (14.454)$$

Substitution of Eqs. (14.443) and (14.453) into Eq. (14.454) gives

$$d_{C-H_{benzene},H_2MO} = 1.24678a_0 = 6.59767\,X\,10^{-11}\ m \quad (14.455)$$

The distance $d_{C-H_{benzene}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{benzene}2sp^3HO} = d_{C-H_{benzene},H_2MO} - c' \quad (14.456)$$

Substitution of Eqs. (14.444) and (14.455) into Eq. (14.456) gives

$$d_{C-H_{benzene}2sp^3HO} = 0.21379a_0 = 1.13131\,X\,10^{-11}\ m \quad (14.457)$$

The basis set of benzene, the ethylene molecule, is planar with bond angles of approximately 120° (Eqs. (14.298-14.302)). To form a closed ring of equivalent planar bonds, the $C=C$ bonds of benzene form a planar hexagon. The bond angle $\theta_{C=C=C}$ between the internuclear axis of any two adjacent $C=C$ bonds is

$$\theta_{C=C=C} = 120° \quad (14.458)$$

The bond angle $\theta_{C=C-H}$ between the internuclear axis of each $C=C$ bond and the corresponding H atom of each CH group is

$$\theta_{C=C-H} = 120° \quad (14.459)$$

The experimental angle between the $C=C=C$ bonds is [13-15]

$$\theta_{C=C=C} = 120° \quad (14.460)$$

The experimental angle between the $C=C-H$ bonds is [13-15]

$$\theta_{C=C-H} = 120° \quad (14.461)$$

The C_6H_6 MO shown in Figure 47 was rendered using these parameters.

The charge-density in the $C=C$-bond MO is increased by a factor of 0.25 per bond with the formation of the $C_{benzene}2sp^3$ HOs each having a smaller radius. Using the orbital

composition of the CH groups (Eq. (14.439)) and the $C=C$-bond MO (Eq. (14.416), the radii of $C1s=0.17113a_0$ (Eq. (10.51)) and $C_{benzene}2sp^3=0.79597a_0$ (Eq. (14.520)) shells, and the parameters of the $C=C$-bond (Eqs. (13.3-13.4), (14.424-14.426), and (14.428-14.438)), the parameters of the $C-H$-bond MOs (Eqs. (13.3-13.4), (14.443-14.445), and (14.447-14.457)), and the bond-angle parameters (Eqs. (14.458-14.459)), the charge-density of the C_6H_6 MO comprising the linear combination of six sets of $C-H$-bond MOs with bridging $\overset{3e}{C=C}$-bond MOs is shown in Figure 47. Each $C-H$-bond MO comprises a H_2-type ellipsoidal MO and a $C_{benzene}2sp^3$ HO having the dimensional diagram shown in Figure 46. The $C=C$-bond MO comprises a H_2-type ellipsoidal MO bridging two sets of two $C_{benzene}2sp^3$ HOs having the dimensional diagram shown in Figure 45.

ENERGIES OF THE CH GROUPS

The energies of each CH group of benzene are given by the substitution of the semiprincipal axes (Eqs. (14.443-14.444) and (14.447)) into the energy equations of hydrogen carbide (Eqs. (13.449-13.453)), with the exception that $E_T\left(C=C,2sp^3\right)$ (Eq. (14.247)) is subtracted from $E_T\left(CH\right)$ in Eq. (13.453):

$$V_e=\left(0.91771\right)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-37.10024\ eV \tag{14.462}$$

$$V_p=\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=13.17125\ eV \tag{14.463}$$

$$T=\left(0.91771\right)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=11.58941\ eV \tag{14.464}$$

$$V_m=\left(0.91771\right)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-5.79470\ eV \tag{14.465}$$

$$E_{T_{benzene}}\left(CH\right)=\left(\begin{array}{l}-\frac{e^2}{8\pi\varepsilon_0c'}\left[\left(0.91771\right)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-14.63489\ eV-\left(-1.13379\ eV\right)\end{array}\right)=-31.63539\ eV \tag{14.466}$$

where $E_{T_{benzene}}\left(CH\right)$ is given by Eq. (14.440) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C-H$-bond MO, $E_{T_{benzene}}(C-H)$, is given by the sum of $0.5E_T\left(C=C,2sp^3\right)$, the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the formation of the corresponding $C=C$-bond MO (Eq. (14.247)), and $E_{T_{benzene}}(CH)$, the σ MO contribution given by Eq. (14.441):

$$\begin{aligned} E_{T_{benzene}}(C-H) &= (0.5)E_T\left(C=C,2sp^3\right)+E_{T_{benzene}}(CH) \\ &= \left(\begin{array}{l}(0.5)(-1.13379\ eV)+ \\ \left(-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\right) \\ -14.63489\ eV-(-1.13379\ eV)\end{array}\right) \\ &= (0.5)(-1.13379\ eV)+(-31.63537\ eV) \\ &= -32.20226\ eV \end{aligned} \tag{14.467}$$

VIBRATION OF THE ^{12}CH GROUPS

The vibrational energy levels of CH in benzene may be solved using the methods given in the Vibration and Rotation of CH section.

THE DOPPLER ENERGY TERMS OF THE ^{12}CH GROUPS

The equations of the radiation reaction force of the CH groups in benzene are the same as those of the hydrogen carbide radical with the substitution of the CH-group parameters. Using Eq. (13.477), the angular frequency of the reentrant oscillation in the transition state is

$$\omega=\sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}}=2.64826\,X\,10^{16}\ rad/s \tag{14.468}$$

where b is given by Eq. (14.447). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K=\hbar\omega=\hbar 2.64826\,X\,10^{16}\ rad/s=17.43132\ eV \tag{14.469}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.469) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(17.43132\ eV)}{m_e c^2}} = -0.26130\ eV \tag{14.470}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.470) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition, $\overline{E}_{benzene\ osc}\left({}^{12}CH\right)$ per bond is

$$\overline{E}_{benzene\ osc}\left({}^{12}CH\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.471}$$

$$\overline{E}_{benzene\ osc}\left({}^{12}CH\right) = -0.26130\ eV + \frac{1}{2}(0.35532\ eV) = -0.08364\ eV \tag{14.472}$$

TOTAL AND BOND ENERGIES OF THE ${}^{12}CH$ GROUPS

$E_{benzeneT+osc}\left({}^{12}CH\right)$, the total energy of each ${}^{12}CH$ group including the Doppler term, is given by the sum of $E_{T_{benzene}}(C-H)$ (Eq. (14.467)) and $\overline{E}_{benzene\ osc}\left({}^{12}CH\right)$ given by Eq. (14.472):

$$E_{benzeneT+osc}(CH) = \begin{pmatrix}\left(V_e + T + V_m + V_p + E\left(C,2sp^3\right) - E_T\left(C=C,2sp^3\right)\right)\\ +0.5E_T\left(C=C,2sp^3\right) + \overline{E}_{benzene\ osc}\left({}^{12}CH\right)\end{pmatrix} \tag{14.473}$$
$$= E_{T_{benzene}}(C-H) + \overline{E}_{benzene\ osc}\left({}^{12}CH\right)$$

$$E_{benzeneT+osc}\left({}^{12}CH\right) = \left\{\begin{pmatrix}\frac{-e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\ -14.63489\ eV-(-1.13379\ eV)\end{pmatrix} - 0.5(1.13379\ eV)\right\}$$
$$\left\{-\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}m_e}}{m_e c^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\right\}$$
$$= -32.20226\ eV - \left(0.26130\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{14.474}$$

From Eqs. (14.472-14.474), the total energy of each ${}^{12}CH$ is

$$E_{benzeneT+osc}\left({}^{12}CH\right) = -32.20226\ eV + \overline{E}_{benzene\ osc}\left({}^{12}CH_2\right)$$
$$= -32.20226\ eV - \left(0.26130\ eV - \frac{1}{2}(0.35532\ eV)\right) \quad (14.475)$$
$$= -32.28590\ eV$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

As in the case of ${}^{12}CH_2$, ${}^{14}NH$, and acetylene, the dissociation of the $C=C$ bonds forms three unpaired electrons per central atom wherein the magnetic moments cannot all cancel. The energy per atom $E(magnetic)$ is given by Eq. (13.524). Thus, the bond dissociation energy of each CH group of the linear combination to form benzene, $E_{D_{benzene}}\left({}^{12}CH\right)$, is given by the sum of the total energies of the $C2sp^3$ HO and the hydrogen atom minus the sum of $E_{benzeneT+osc}\left({}^{12}CH\right)$ and $E(magnetic)$ given by Eq. (13.524):

$$E_{D_{benzene}}\left({}^{12}CH\right) = E\left(C,2sp^3\right) + E(H) - \left(E_{benzeneT+osc}\left({}^{12}CH\right) + E(magnetic)\right) \quad (14.476)$$

$E\left(C,2sp^3\right)$ is given by Eq. (13.428), $E_D(H)$ is given by Eq. (13.154), and $E(magnetic)$ is given by Eq. (13.524). Thus, $E_{D_{benzene}}\left({}^{12}CH\right)$ given by Eqs. (13.154), (13.428), (13.524), (14.475), and (14.476) is

$$E_{D_{benzene}}\left({}^{12}CH\right) = -\left(14.63489\ eV + 13.59844\ eV\right) - \left(E_{benzeneT+osc}(CH) + E(magnetic)\right)$$
$$= -28.23333\ eV - \left(-32.28590\ eV + 0.14803\ eV\right) \quad (14.477)$$
$$= 3.90454\ eV$$

SUM OF THE ENERGIES OF THE $C=C$ σ MO ELEMENT AND THE HOs OF BENZENE

The energy components of V_e, V_p, T, V_m, and E_T of the $C=C$-bond MO of benzene are the same as those of the CH_2CH_2 MO except that the hybridization factor is given by Eq. (14.417). The energies of each $C=C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.424-14.425) and (14.428)) into energy equations of the CH_2CH_2 MO (Eqs. (14.319-14.323)), with the exception that the hybridization factor is 0.85252 (Eq. (14.417)):

$$V_e = 2(0.85252)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -101.12679\ eV \quad (14.478)$$

$$V_p = 2\frac{e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 20.69825\ eV \tag{14.479}$$

$$T = 2(0.85252)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 34.31559\ eV \tag{14.480}$$

$$V_m = 2(0.85252)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -17.15779\ eV \tag{14.481}$$

$$E_T(C=C,\sigma) = -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] = -63.27075\ eV \tag{14.482}$$

where $E_T(C=C,\sigma)$ is the total energy of the $C=C$ σ MO given by Eq. (14.421) which is reiteratively matched to two times Eq. (13.75) within five-significant-figure round off error.

The total energy of the $C=C$-bond MO, $E_T(C=C)$, is given by the sum of two times $E_T(C=C,2sp^3)$, the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of the $C=C$-bond MO (Eq. (14.247)), and $E_T(C=C,\sigma)$, the σ MO contribution given by Eq. (14.422):

$$\begin{aligned} E_T(C=C) &= 2E_T(C=C,2sp^3)+E_T(C=C,\sigma) \\ &= \left(\begin{array}{l} 2(-1.13380\ eV)+ \\ \left(-\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\right) \end{array}\right) \\ &= 2(-1.13380\ eV)+(-63.27074\ eV) = -65.53833\ eV \end{aligned} \tag{14.483}$$

which is the same $E_T(C=C,\sigma)$ of ethylene given by Eq. (14.324).

VIBRATION OF BENZENE

The $C=C$ vibrational energy levels of C_6H_6 may be solved as six sets of equivalent coupled harmonic oscillators where each C is a further coupled to the corresponding $C-H$ oscillator by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $C=C$-BOND MO ELEMENT

OF BENZENE

The equations of the radiation reaction force of the $C=C$ -bond MO of benzene are given by Eq. (13.142), except the force-constant factor is $(0.85252)0.5$ based on the force constant k' of Eq. (14.418), and the $C=C$ -bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{0.85252\frac{(0.5)e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 4.97272\,X\,10^{16}\ rad/s \tag{14.484}$$

where b is given by Eq. (14.428). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 4.97272\,X\,10^{16}\ rad/s = 32.73133\ eV \tag{14.485}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.485) for $\overline{E}_K$ gives the Doppler energy of the electrons for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63536831\ eV\sqrt{\frac{2e(32.73133\ eV)}{m_e c^2}} = -0.35806\ eV \tag{14.486}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of the $C=C$ -bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.486) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of the $C=C$ bond. Using the experimental $C=C$ $E_{vib}(\upsilon_{16})$ of 1584.8 cm^{-1} $(0.19649\ eV)$ [16] for $\overline{E}_{Kvib}$ of the transition state having two bonds, $\overline{E}'_{osc}(C=C,\sigma)$ per bond is

$$\overline{E}'_{osc}(C=C,\sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.487}$$

$$\overline{E}'_{osc}(C=C,\sigma) = -0.35806\ eV + \frac{1}{2}(0.19649\ eV) = -0.25982\ eV \tag{14.488}$$

Given that the vibration and reentrant oscillation is for two $C-C$ bonds of each $C=C$ double bond, $\bar{E}_{benzene\ osc}(C=C,\sigma)$, is:

$$\bar{E}_{benzene\ osc}(C=C,\sigma)=2\left(\bar{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)=2\left(-0.35806\ eV+\frac{1}{2}(0.19649\ eV)\right)=-0.51963\ eV \tag{14.489}$$

TOTAL ENERGIES OF THE $C=C$-BOND MO ELEMENT OF BENZENE

$E_{T+osc}(C=C)$, the total energy of the $C=C$-bond MO of benzene including the Doppler term, is given by the sum of $E_T(C=C)$ (Eq. (14.483)) and $\bar{E}_{benzene\ osc}(C=C,\sigma)$ given by Eq. (14.489):

$$\begin{aligned}E_{T+osc}(C=C)&=V_e+T+V_m+V_p+2E_T\left(C=C,2sp^3\right)+\bar{E}_{benzene\ osc}(C=C,\sigma)\\&=E_T(C=C,\sigma)+2E_T\left(C=C,2sp^3\right)+\bar{E}_{benzene\ osc}(C=C,\sigma)\\&=E_T(C=C)+\bar{E}_{benzene\ osc}(C=C,\sigma)\end{aligned} \tag{14.490}$$

$$E_{T+osc}(C=C)=\left\{\begin{array}{l}\left(\frac{-2e^2}{8\pi\varepsilon_0 c'}\left[(0.85252)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+2E_T\left(C=C,2sp^3\right)\right)\\-2\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{(0.85252)\frac{1}{2}\frac{e^2}{4\pi\varepsilon_o b^3}}{m_e}}}{m_e c^2}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\} \tag{14.491}$$

$$=-65.53833\ eV-2\left(0.35806\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

From Eqs. (14.489-14.491), the total energy of the $C=C$-bond MO is

$$\begin{aligned}E_{T+osc}(C=C)&=-63.27074\ eV+2E_T\left(C=C,2sp^3\right)+\bar{E}_{benzene\ osc}(C=C,\sigma)\\&=-63.27074\ eV+2(-1.13380\ eV)-2\left(0.35806\ eV-\frac{1}{2}(0.19649\ eV)\right)\\&=-66.05796\ eV\end{aligned} \tag{14.492}$$

where the experimental E_{vib} was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

TOTAL BOND DISSOCIATION ENERGY OF BENZENE

Ethylene serves as a basis element for the $C=C$ bonding of benzene wherein each of the six $\overset{3e}{C=C}$ bonds of benzene comprises $(0.75)(4)=3$ electrons according to Eq. (14.416). The total energy of the bonds of the eighteen electrons of the $\overset{3e}{C=C}$ bonds of benzene, $E_T\left(C_6H_6,\overset{3e}{C=C}\right)$, is given by (6)(0.75) times $E_{T+osc}(C=C)$ (Eq. (14.492)), the total energy of the $C=C$ -bond MO of benzene including the Doppler term, minus eighteen times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the double $C=C$ bonds. Thus, the total energy of the six $\overset{3e}{C=C}$ bonds of benzene is

$$\begin{aligned} E_T\left(C_6H_6,\overset{3e}{C=C}\right) &= (6)(0.75)E_{T+osc}(C=C)-18E\left(C,2sp^3\right) \\ &= (6)(0.75)(-66.05796\ eV)-18(-14.63489\ eV) \\ &= -297.26081\ eV-(-263.42798\ eV) \\ &= -33.83284\ eV \end{aligned} \tag{14.493}$$

Each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each $C-H$ bond, $-E_{D_{benzene}}\left({}^{12}CH\right)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T\left(C_6H_6,C-H\right)$, is given by

$$E_T\left(C_6H_6,C-H\right)=(6)\left(-E_{D_{benzene}}\left({}^{12}CH\right)\right)=6(-3.90454\ eV)=-23.42724\ eV \tag{14.494}$$

The total bond dissociation energy of benzene, $E_D\left(C_6H_6\right)$, is given by the negative sum of $E_T\left(C_6H_6,\overset{3e}{C=C}\right)$ (Eq. (14.493)) and $E_T\left(C_6H_6,C-H\right)$ (Eq. (14.494)):

$$\begin{aligned} E_D\left(C_6H_6\right) &= -\left(E_T\left(C_6H_6,\overset{3e}{C=C}\right)+E_T\left(C_6H_6,C-H\right)\right) \\ &= -\left((-33.83284\ eV)+(-23.42724\ eV)\right) \\ &= 57.2601\ eV \end{aligned} \tag{14.495}$$

The experimental total bond dissociation energy of benzene, $E_T\left(C_6H_6\right)$, is given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(benzene(gas)\right)$) and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C(gas)\right)$) and hydrogen ($\Delta H_f\left(H(gas)\right)$) atoms. The heats of formation are [17-18]

$$\Delta H_f\left(benzene(gas)\right)=82.9\ kJ/mole\ \left(0.8592\ eV/molecule\right) \tag{14.496}$$

$$\Delta H_f\left(C(gas)\right)=716.68\ kJ/mole\ \left(7.42774\ eV/molecule\right) \quad (14.497)$$

$$\Delta H_f\left(H(gas)\right)=217.998\ kJ/mole\ \left(2.259353\ eV/molecule\right) \quad (14.498)$$

Thus, the total bond dissociation energy of benzene, $E_D\left(C_6H_6\right)$, is

$$\begin{aligned} E_D\left(C_6H_6\right)-E_T\left(C_6H_6\right) &= -\left(\Delta H_f\left(benzene(gas)\right)-\left(6\Delta H_f\left(C(gas)\right)+6\Delta H_f\left(H(gas)\right)\right)\right) \\ &= -\left(0.8592\ eV-6\left(7.42774\ eV+2.259353\ eV\right)\right) \\ &= 57.26\ eV \end{aligned} \quad (14.499)$$

where $E_T\left(C_6H_6\right)$ is the total energy of the bonds. The results of the determination of bond parameters of C_6H_6 are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

CONTINUOUS-CHAIN ALKANES (C_nH_{2n+2}, $n=3,4,5...\infty$)

The continuous chain alkanes, C_nH_{2n+2}, are the homologous series comprising terminal methyl groups at each end of the chain with $n-2$ methylene (CH_2) groups in between:

$$CH_3\left(CH_2\right)_{n-2}CH_3 \quad (14.500)$$

C_nH_{2n+2} can be solved using the same principles as those used to solve ethane and ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three H AOs combine with three carbon $2sp^3$ HOs and two H AOs combine with two carbon $2sp^3$ HOs to form each methyl and methylene group, respectively, where each bond comprises a H_2-type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The CH_3 and CH_2 groups bond by forming H_2-type MOs between the remaining $C2sp^3$ HOs on the carbons such that each carbon forms four bonds involving its four $C2sp^3$ HOs.

FORCE BALANCE OF THE $C-C$-BOND MOs OF CONTINUOUS-CHAIN ALKANES

C_nH_{2n+2} comprises a chemical bond between two terminal CH_3 radicals and $n-2$ CH_2 radicals wherein each methyl and methylene radical comprises three and two chemical bonds, respectively, between carbon and hydrogen atoms. The solution of the parameters of CH_3 is given in the Methyl Radical (CH_3) section. The solution of the parameters of CH_2 is given in the Dihydrogen Carbide Radical (CH_2) section and follows the same procedure. Each $C-H$ bond having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the linear combination of 75% H_2-type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.429):

$$1\,C2sp^3 + 0.75\,H_2\ MO \rightarrow C-H\ MO \tag{14.501}$$

The proton of the H atom and the nucleus of the C atom are along each internuclear axis and serve as the foci. As in the case of H_2, each of the $C-H$-bond MOs is a prolate spheroid with the exception that the ellipsoidal MO surface cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell since it is energetically unfavorable. Thus, each MO surface comprises a prolate spheroid at the H proton that is continuous with the $C2sp^3$ shell at the C atom whose nucleus serves as the other focus. The electron configuration and the energy, $E\left(C,2sp^3\right)$, of the $C2sp^3$ shell is given by Eqs. (13.422) and (13.428), respectively. The central paramagnetic force due to spin of each $C-H$ bond is provided by the spin-pairing force of the CH_3 or CH_2 MO that has the symmetry of an s orbital that superimposes with the $C2sp^3$ orbitals such that the corresponding angular momenta are unchanged. The energies of each CH_3 and CH_2 MO involve each $C2sp^3$ and each $H1s$ electron with the formation of each $C-H$ bond. The sum of the energies of the H_2-type ellipsoidal MOs is matched to that of the $C2sp^3$ shell. The force balance of the $C-H$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.139) and the energy matching condition between the $C2sp^3$-HO components of the MO.

The CH_3 and CH_2 groups form $C-C$ bonds comprising H_2-type MOs between the remaining $C2sp^3$ HOs on the carbons such that each carbon forms four bonds involving its four $C2sp^3$ HOs. The sharing of electrons between any two $C2sp^3$ HOs to form a molecular orbital (MO) comprising two spin-paired electrons permits each $C2sp^3$ HO to decrease in radius and energy. As in the case of the $C-H$ bonds, each $C-C$-bond MO is a prolate-spheroidal-MO surface that cannot extend into $C2sp^3$ HO for distances shorter than the radius of the $C2sp^3$ shell of each atom. Thus, the MO surface comprises a partial prolate spheroid in between the carbon nuclei and is continuous with the $C2sp^3$ shell at each C atom. The energy of the H_2-type ellipsoidal MO is matched to that of the $C2sp^3$ shell. As in the case of previous examples of energy-matched MOs such as the $C-C$-bond MO of ethane, each $C-C$-bond MO of C_nH_{2n+2} must comprise 75% of a H_2-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Thus, the $C-C$-bond MO must comprise two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the two $C2sp^3$ HOs:

$$2\,C2sp^3 + 0.75\,H_2\ MO \rightarrow C-C-bond\ MO \tag{14.502}$$

The linear combination of the H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution from each $C2sp^3$ HO to the $C-C$-bond MO to achieve an energy minimum. The force balance of the $C-C$-bond MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.502) and the energy matching condition between the $C2sp^3$-HO components of the MO.

Before bonding, the $2sp^3$ hybridized orbital arrangement of each carbon atom is given by Eq. (14.140). The sum $E_T\left(C,2sp^3\right)$ of calculated energies of C, C^+, C^{2+}, and C^{3+} is given by Eq. (14.141). The radius r_{2sp^3} of the $C2sp^3$ shell is given by Eq. (14.142). The Coulombic energy $E_{Coulomb}\left(C,2sp^3\right)$ and the energy $E\left(C,2sp^3\right)$ of the outer electron of the $C2sp^3$ shell are given by Eqs. (14.143) and (14.146), respectively.

The formation of each $C-C$ bond of C_nH_{2n+2} further requires that the energy of all

H_2-type prolate spheroidal MOs (σ MOs) be matched at all $C2sp^3$ HOs since they are continuous throughout the molecule. Thus, the energy of each $C2sp^3$ HO must be a linear combination of that of the CH_3 and CH_2 groups that serve as basis elements. Each CH_3 forms one $C-C$ bond, and each CH_2 group forms two. Thus, the energy of each $C2sp^3$ HO of each CH_3 and CH_2 group alone is given by that in ethane and ethylene, respectively. The parameters of ethane and ethylene are given by Eqs. (14.147-14.151) and (14.244-14.247), respectively. The alkane parameters can be determined by first reviewing those of ethane and ethylene.

With the formation of the $C-C$-bond MO of ethane from two methyl radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146), the total energy of the state is given by the sum over the four electrons. The sum $E_T\left(C_{ethane},2sp^3\right)$ of calculated energies of $C2sp^3$, C^+, C^{2+}, and C^{3+} given by Eq. (14.147), is

$$\begin{aligned} E_T\left(C_{ethane},2sp^3\right) &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + E\left(C,2sp^3\right)\right) \\ &= -\left(64.3921\ eV + 48.3125\ eV + 24.2762\ eV + 14.63489\ eV\right) \\ &= -151.61569\ eV \end{aligned} \quad (14.503)$$

where $E\left(C,2sp^3\right)$ is the sum of the energy of C, $-11.27671\ eV$, and the hybridization energy. The orbital-angular-momentum interactions also cancel such that the energy of the $E_T\left(C_{ethane},2sp^3\right)$ is purely Coulombic.

The sharing of electrons between two $C2sp^3$ HOs to form a $C-C$-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $C2sp^3$ HO donates an excess of 25% of its electron density to the $C-C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethane molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethane2sp^3}$ of the $C2sp^3$ shell of ethane may be calculated from the Coulombic energy using Eq. (10.102):

$$r_{ethane2sp^3} = \left(\sum_{n=2}^{5}(Z-n)-0.25\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = \frac{9.75e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} = 0.87495a_0 \quad (14.504)$$

Using Eqs. (10.102) and (14.504), the Coulombic energy $E_{Coulomb}\left(C_{ethane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E_{Coulomb}\left(C_{ethane},2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.87495a_0}=-15.55033\ eV \qquad (14.505)$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.505), the energy $E\left(C_{ethane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E\left(C_{ethane},2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{ethane2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}=-15.55033\ eV+0.19086\ eV=-15.35946\ eV \qquad (14.506)$$

Thus, $E_T\left(C-C,2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C-C$-bond MO is given by the difference between Eq. (14.146) and Eq. (14.506):

$$E_T\left(C-C,2sp^3\right)=E\left(C_{ethane},2sp^3\right)-E\left(C,2sp^3\right)=-15.35946\ eV-\left(-14.63489\ eV\right)=-0.72457\ eV \qquad (14.507)$$

Next, consider the formation of the $C=C$-bond MO of ethylene from two CH_2 radicals, each having a $C2sp^3$ electron with an energy given by Eq. (14.146). The sum $E_T\left(C_{ethylene},2sp^3\right)$ of calculated energies of $C2sp^3$, C^+, C^{2+}, and C^{3+} is given by Eq. (14.147). The sharing of electrons between two pairs of $C2sp^3$ HOs to form a $C=C$-bond MO permits each participating HO to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each participating $C2sp^3$ HO donates an excess of 25% of its electron density to the $C=C$-bond MO to form an energy minimum. By considering this electron redistribution in the ethylene molecule as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius $r_{ethylene2sp^3}$ of the $C2sp^3$ shell of ethylene may be calculated from the Coulombic energy using Eqs. (10.102) and (14.147):

$$r_{ethylene2sp^3} = \left(\sum_{n=2}^{5}(Z-n)-0.5\right)\frac{e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)}$$
$$= \frac{9.5e^2}{8\pi\varepsilon_0\left(e151.61569\ eV\right)} \qquad (14.508)$$
$$= 0.85252a_0$$

where $Z=6$ for carbon. Using Eqs. (10.102) and (14.508), the Coulombic energy $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E_{Coulomb}\left(C_{ethylene}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}} = \frac{-e^2}{8\pi\varepsilon_0 0.85252a_0} = -15.95955\ eV \qquad (14.509)$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.509), the energy $E\left(C_{ethylene}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E\left(C_{ethylene}, 2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{ethylene2sp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3} = -15.95955\ eV + 0.19086\ eV = -15.76868\ eV \qquad (14.510)$$

Thus, $E_T\left(C=C, 2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of the $C=C$ -bond MO is given by the difference between Eq. (14.146) and Eq. (14.510):

$$E_T\left(C=C, 2sp^3\right) = E\left(C_{ethylene}, 2sp^3\right) - E\left(C, 2sp^3\right)$$
$$= -15.76868\ eV - \left(-14.63489\ eV\right) \qquad (14.511)$$
$$= -1.13380\ eV$$

To meet the energy matching condition for all σ MOs at all $C2sp^3$ HOs, the energy $E\left(C_{alkane}, 2sp^3\right)$ of the outer electron of the $C2sp^3$ shell of each alkane carbon atom must be the average of $E\left(C_{ethane}, 2sp^3\right)$ (Eq. (14.506)) and $E\left(C_{ethylene}, 2sp^3\right)$ (Eq. (14.510)):

$$E\left(C_{alkane}, 2sp^3\right) = \frac{E\left(C_{ethane}, 2sp^3\right) + E\left(C_{ethylene}, 2sp^3\right)}{2}$$
$$= \frac{\left(-15.35946\ eV\right) + \left(-15.76868\ eV\right)}{2} \qquad (14.512)$$
$$= -15.56407\ eV$$

And, $E_{T_{alkane}}\left(C-C,2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of each $C-C$-bond MO, must be the average of $E_T\left(C-C,2sp^3\right)$ (Eq. (14.507)) and $E_T\left(C=C,2sp^3\right)$ (Eq. (14.511)):

$$\begin{aligned} E_{T_{alkane}}\left(C-C,2sp^3\right) &= \frac{E_T\left(C-C,2sp^3\right)+E_T\left(C=C,2sp^3\right)}{2} \\ &= \frac{\left(-0.72457\ eV\right)+\left(-1.13379\ eV\right)}{2} \\ &= -0.92918\ eV \end{aligned} \tag{14.513}$$

Using Eq. (10.102), the radius $r_{alkane2sp^3}$ of the $C2sp^3$ shell of each carbon atom of C_nH_{2n+2} may be calculated from the Coulombic energy using the initial energy $E_{Coulomb}\left(C,2sp^3\right)=-14.82575\ eV$ (Eq. (14.143)) and $E_{T_{alkane}}\left(C-C,2sp^3\right)$ Eq. (14.513)), the energy change of each $C2sp^3$ shell with the formation of each $C-C$-bond MO. Consider the case of a methyl carbon which donates $E_{T_{alkane}}\left(C-C,2sp^3\right)$ Eq. (14.513)) to a single $C-C$ bond:

$$\begin{aligned} r_{alkane2sp^3} &= \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+E_{T_{alkane}}\left(C-C,2sp^3\right)\right)} \\ &= \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+e0.92918\ eV\right)} \\ &= 0.86359a_0 \end{aligned} \tag{14.514}$$

Using Eqs. (10.102) and (14.514), the Coulombic energy $E_{Coulomb}\left(C_{alkane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E_{Coulomb}\left(C_{alkane},2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{alkane2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.86359a_0}=-15.75493\ eV \tag{14.515}$$

During hybridization, one of the spin-paired $2s$ electrons is promoted to $C2sp^3$ shell as an unpaired electron. The energy for the promotion is the magnetic energy given by Eq. (14.145). Using Eqs. (14.145) and (14.515), the energy $E\left(C_{alkane},2sp^3\right)$ of the outer electron of the $C2sp^3$ shell is

$$E\left(C_{alkane},2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{alkane2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}=-15.75493\ eV+0.19086\ eV=-15.56407\ eV$$

(14.516)

Thus, $E_{T_{alkane}}\left(C-C,2sp^3\right)$, the energy change of each $C2sp^3$ shell with the formation of each $C-C$-bond MO is given by the difference between Eq. (14.146) and Eq. (14.516):

$$E_{T_{alkane}}\left(C-C,2sp^3\right)=E\left(C_{alkane},2sp^3\right)-E\left(C,2sp^3\right)=-15.56407\ eV-\left(-14.63489\ eV\right)=-0.92918\ eV \quad (14.517)$$

which agrees with Eq. (14.513).

The energy contribution due to the charge donation at each carbon superimposes linearly. In general, the radius r_{mol2sp^3} of the $C2sp^3$ HO of a carbon atom of a group of a given molecule is calculated using Eq. (14.514) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$\begin{aligned} r_{mol2sp^3} &= \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{mol}}\left(MO,2sp^3\right)\right)} \\ &= \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+\sum\left|E_{T_{mol}}\left(MO,2sp^3\right)\right|\right)} \end{aligned} \quad (14.518)$$

The $C2sp^3$ HO of each methyl group of an alkane contributes $-0.92918\ eV$ to the corresponding single $C-C$ bond; thus, the corresponding $C2sp^3$ HO radius is given by Eq. (14.514). The $C2sp^3$ HO of each methylene group of C_nH_{2n+2} contributes $-0.92918\ eV$ to each of the two corresponding $C-C$ bond MOs. Thus, the radius of each methylene group of an alkane is given by

$$\begin{aligned} r_{alkaneC_{methylene}2sp^3} &= \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{alkane}}\left(methylene\ C-C,2sp^3\right)\right)} \\ &= \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+e0.92918\ eV+e0.92918\ eV\right)} \\ &= 0.81549a_0 \end{aligned} \quad (14.519)$$

As in the case with ethane, the H_2-type ellipsoidal MO comprises 75% of the $C-C$-bond MO shared between two $C2sp^3$ HOs corresponding to the electron charge density in Eq. (11.65) of $\frac{-0.75e}{2}$. But, the additional 25% charge-density contribution to the $C-C$-bond MO causes the electron charge density in Eq. (11.65) to be is given by $\frac{-e}{2}=-0.5e$.

Thus, the force constant k' to determine the ellipsoidal parameter c' in terms of the central force of the foci is given by Eq. (14.152). The distance from the origin of the $C-C$-bond MO to each focus c' is given by Eq. (14.153). The internuclear distance from is given by Eq. (14.154). The length of the semiminor axis of the prolate spheroidal $C-C$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of the $C-C$-bond MO. Since the $C-C$-bond MO comprises a H_2-type-ellipsoidal MO that transitions to the $C_{alkane}2sp^3$ HO of each carbon, the energy $E\left(C_{alkane},2sp^3\right)$ in Eq. (14.512) adds to that of the H_2-type ellipsoidal MO to give the total energy of the $C-C$-bond MO. From the energy equation and the relationship between the axes, the dimensions of the $C-C$-bond MO are solved. Similarly, $E\left(C_{alkane},2sp^3\right)$ is added to the energy of the H_2-type ellipsoidal MO of each $C-H$ bond of the methyl and methylene groups to give their total energy. From the energy equation and the relationship between the axes, the dimensions of the equivalent $C-H$-bond MOs of the methyl and methylene groups in the alkane are solved.

The general equations for the energy components of V_e, V_p, T, V_m, and E_T of each $C-C$-bond MO are the same as those of the CH MO except that energy of the $C_{alkane}2sp^3$ HO is used. The energy components at each carbon atom superimpose linearly and may be treated independently. Since each prolate spheroidal H_2-type MO transitions to the $C_{alkane}2sp^3$ HO of each corresponding carbon of the bond and the energy of the $C_{alkane}2sp^3$ shell treated independently must remain constant and equal to the $E\left(C_{alkane},2sp^3\right)$ given by Eq. (14.512), the total energy $E'_{T_{alkane}}\left(C-C,\sigma\right)$ of the σ component of each $C-C$-bond MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{alkane}2sp^3$ HO and the H_2-type ellipsoidal MO that forms the σ component of the $C-C$-bond MO as given by Eq. (14.502) with the electron charge redistribution. The total number of $C-C$ bonds in C_nH_{2n+2} is $n-1$. Using Eqs. (13.431) and (14.512), $E_{T_{alkane}}\left(C-C,\sigma\right)$ of the $n-1$ bonds is given by

$$E_{T_{alkane}}(C-C,\sigma)=(n-1)\left(E_T+E\left(C_{alkane},2sp^3\right)\right)$$
$$=(n-1)\left(-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV\right) \quad (14.520)$$

To match the boundary condition that the total energy of each H_2-type ellipsoidal MO is given by Eqs. (11.212) and (13.75), $E_{T_{alkane}}(C-C,\sigma)$ given by Eq. (14.520) is set equal to $(n-1)$ times Eq. (13.75):

$$E_{T_{alkane}}(C-C,\sigma)=$$
$$(n-1)\left(\begin{matrix}-\frac{e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\ -15.56407\ eV\end{matrix}\right)=(n-1)(-31.63536831\ eV) \quad (14.521)$$

From the energy relationship given by Eq. (14.521) and the relationship between the axes given by Eqs. (14.153-14.154) and (13.62-13.63), the dimensions of the $C-C$-bond MO can be solved.

Substitution of Eq. (14.153) into Eq. (14.521) gives

$$\frac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right]=e16.07130 \quad (14.522)$$

The most convenient way to solve Eq. (14.522) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=2.12499a_0=1.12450\,X\,10^{-10}\ m \quad (14.523)$$

Substitution of Eq. (14.523) into Eq. (14.155) gives

$$c'=1.45774a_0=7.71400\,X\,10^{-11}\ m \quad (14.524)$$

The internuclear distance given by multiplying Eq. (14.524) by two is

$$2c'=2.91547a_0=1.54280\,X\,10^{-10}\ m \quad (14.525)$$

The experimental $C-C$ bond distance of propane is [3]

$$2c'=1.532\,X\,10^{-10}\ m \quad (14.526)$$

The experimental $C-C$ bond distance of butane is [3]

$$2c'=1.531\,X\,10^{-10}\ m \quad (14.527)$$

Substitution of Eqs. (14.523-14.524) into Eq. (13.62) gives

$$b=c=1.54616a_0=8.18192\,X\,10^{-11}\ m \quad (14.528)$$

Substitution of Eqs. (14.523-14.524) into Eq. (13.63) gives

$$e = 0.68600 \tag{14.529}$$

The nucleus of the C atoms comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{alkane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where for methylene bonds $r_n = r_{alkane2sp^3} = r_{methylene2sp^3}$=$0.81549a_0$ is the radius of the $C_{alkane}2sp^3$ shell given by Eq. (14.519). Substitution of Eqs. (14.523-14.524) into Eq. (13.261) gives

$$\theta' = 56.41° \tag{14.530}$$

Then, the angle $\theta_{C-C_{alkane}2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-C_{alkane}2sp^3HO} = 180° - 56.41° = 123.59° \tag{14.531}$$

as shown in Figure 48.

Consider the right-hand intersection point. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C-C_{alkane},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C_{alkane}2sp^3$ radial vector obeys the following relationship:

$$r_{alkane2sp^3}\sin\theta_{C-C_{alkane}2sp^3HO} = 0.81549a_0\sin\theta_{C-C_{alkane}2sp^3HO} = b\sin\theta_{C-C_{alkane},H_2MO} \tag{14.532}$$

such that

$$\theta_{C-C_{alkane},H_2MO} = \sin^{-1}\frac{0.81549a_0\sin\theta_{C-C_{alkane}2sp^3HO}}{b} = \sin^{-1}\frac{0.81549a_0\sin 123.59°}{b} \tag{14.533}$$

with the use of Eq. (14.531). Substitution of Eq. (14.528) into Eq. (14.533) gives

$$\theta_{C-C_{alkane},H_2MO} = 26.06° \tag{14.534}$$

Then, the distance d_{C-C_{alkane},H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-C_{alkane},H_2MO} = a\cos\theta_{C-C_{alkane},H_2MO} \tag{14.535}$$

Substitution of Eqs. (14.523) and (14.534) into Eq. (14.535) gives

$$d_{C-C_{alkane},H_2MO} = 1.90890a_0 = 1.01015\,X\,10^{-10}\ m \tag{14.536}$$

The distance $d_{C-C_{alkane}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-C_{alkane}2sp^3HO} = d_{C-C_{alkane},H_2MO} - c' \tag{14.537}$$

Substitution of Eqs. (14.524) and (14.536) into Eq. (14.537) gives

$$d_{C-C_{alkane}2sp^3HO} = 0.45117a_0 = 2.38748\,X\,10^{-11}\ m \tag{14.538}$$

FORCE BALANCE OF THE CH_3 MOs OF CONTINUOUS-CHAIN ALKANES

Each of the two CH_3 MOs must comprise three equivalent $C-H$ bonds with each comprising 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.540):

$$3\left[1\,C2sp^3 + 0.75\,H_2\ MO\right] \rightarrow CH_3\ MO \tag{14.539}$$

The force balance of the CH_3 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.539) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH_3 MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the three prolate spheroidal $C-H$-bond MOs comprises an H_2-type-ellipsoidal MO that transitions to the $C_{alkane}2sp^3$ HO of C_nH_{2n+2}, the energy $E\left(C_{alkane},2sp^3\right)$ of Eq. (14.512) adds to that of the three corresponding H_2-type ellipsoidal MOs to give the total energy of the CH_3 MO. From the energy equation and the relationship between the axes, the dimensions of the CH_3 MO are solved.

The energy components of V_e, V_p, T, and V_m are the same as those of methyl radical, three times those of CH corresponding to the three $C-H$ bonds except that energy of the $C_{alkane}2sp^3$ HO is used. Since the each prolate spheroidal H_2-type MO transitions to the $C_{alkane}2sp^3$ HO and the energy of the $C_{alkane}2sp^3$ shell must remain constant and equal to the $E\left(C_{alkane},2sp^3\right)$ given by Eq. (14.512), the total energy $E_{T_{alkane}}\left(CH_3\right)$ of the CH_3 MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{alkane}2sp^3$ HO and the three H_2-type ellipsoidal MOs that forms the CH_3 MO as given by Eq. (14.539). Using Eq. (13.431) or Eq. (13.541), $E_{T_{alkane}}\left(CH_3\right)$ is given by

$$\begin{aligned} E_{T_{alkane}}\left(CH_3\right) &= E_T + E\left(C_{alkane},2sp^3\right) \\ &= -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV \end{aligned} \tag{14.540}$$

$E_{T_{alkane}}\left(CH_3\right)$ given by Eq. (14.540) is set equal to three times the energy of the H_2-type ellipsoidal MO minus two times the Coulombic energy of H given by Eq. (13.542):

$$E_T\left(CH_3\right) = -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV = -67.69450\ eV \tag{14.541}$$

From the energy relationship given by Eq. (14.541) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH_3 MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.541) gives

$$\frac{3e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e52.13044 \tag{14.542}$$

The most convenient way to solve Eq. (14.542) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.64920a_0 = 8.72720\ X\ 10^{-11}\ m \tag{14.543}$$

Substitution of Eq. (14.543) into Eq. (14.60) gives

$$c' = 1.04856a_0 = 5.54872\ X\ 10^{-11}\ m \tag{14.544}$$

The internuclear distance given by multiplying Eq. (14.544) by two is

$$2c' = 2.09711a_0 = 1.10974\ X\ 10^{-10}\ m \tag{14.545}$$

The experimental $C-H$ bond distance of propane is [3]

$$2c' = 1.107\ X\ 10^{-10}\ m \tag{14.546}$$

Substitution of Eqs. (14.543-14.544) into Eq. (14.62) gives

$$b = c = 1.27295 a_0 = 6.73616\ X\ 10^{-11}\ m \tag{14.547}$$

Substitution of Eqs. (14.543-14.544) into Eq. (14.63) gives

$$e = 0.63580 \tag{14.548}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{alkane} 2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{alkane2sp^3} = 0.86359 a_0$ is the radius of the $C_{alkane} 2sp^3$ shell. Substitution of Eqs. (14.543-14.544) into Eq. (13.261) gives

$$\theta' = 77.49° \tag{14.549}$$

Then, the angle $\theta_{C-H_{alkane}\,2sp^3 HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-H_{alkane}\,2sp^3 HO} = 180° - 77.49° = 102.51° \tag{14.550}$$

as shown in Figure 49.

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C-H_{alkane},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C_{alkane} 2sp^3$ radial vector obeys the following relationship:

$$r_{alkane2sp^3} \sin\theta_{C-H_{alkane}\,2sp^3 HO} = 0.86359 a_0 \sin\theta_{C-H_{alkane}\,2sp^3 HO} = b \sin\theta_{C-H_{alkane},H_2MO} \tag{14.551}$$

such that

$$\theta_{C-H_{alkane},H_2MO} = \sin^{-1}\frac{0.86359 a_0 \sin\theta_{C-H_{alkane}\,2sp^3 HO}}{b} = \sin^{-1}\frac{0.86359 a_0 \sin 102.51°}{b} \tag{14.552}$$

with the use of Eq. (14.550). Substitution of Eq. (14.547) into Eq. (14.552) gives

$$\theta_{C-H_{alkane},H_2MO} = 41.48° \tag{14.553}$$

Then, the distance d_{C-H_{alkane},H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane},H_2MO} = a\cos\theta_{C-H_{alkane},H_2MO} \tag{14.554}$$

Substitution of Eqs. (14.543) and (14.553) into Eq. (14.554) gives

$$d_{C-H_{alkane},H_2MO} = 1.23564a_0 = 6.53871\,X\,10^{-11}\ m \tag{14.555}$$

The distance $d_{C-H_{alkane}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane}2sp^3HO} = d_{C-H_{alkane},H_2MO} - c' \tag{14.556}$$

Substitution of Eqs. (14.544) and (14.555) into Eq. (14.556) gives

$$d_{C-H_{alkane}2sp^3HO} = 0.18708a_0 = 9.89999\,X\,10^{-12}\ m \tag{14.557}$$

BOND ANGLE OF THE CH_3 AND CH_2 GROUPS

Each CH_3 MO comprises a linear combination of three $C-H$-bond MOs. Each $C-H$-bond MO comprises the superposition of a H_2-type ellipsoidal MO and the $C_{alkane}2sp^3$ HO. A bond is also possible between the two H atoms of the $C-H$ bonds. Such $H-H$ bonding would decrease the $C-H$ bond strength since electron density would be shifted from the $C-H$ bonds to the $H-H$ bond. Thus, the bond angle between the two $C-H$ bonds is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal H atoms of the $C-H$ bonds is zero. From Eqs. (11.79) and (13.228), the distance from the origin to each focus of the $H-H$ ellipsoidal MO is

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_o}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}} \tag{14.558}$$

The internuclear distance from Eq. (14.558) is

$$2c' = 2\sqrt{\frac{aa_0}{2}} \tag{14.559}$$

The length of the semiminor axis of the prolate spheroidal $H-H$ MO $b=c$ is given by Eq. (14.62).

The bond angle of the CH_3 groups of C_nH_{2n+2} is derived by using the orbital composition and an energy matching factor as in the case with the CH_3 radical. Since each pair of H_2-type ellipsoidal MOs initially comprise 75% of the H electron density of H_2 and

the energy of each H_2-type ellipsoidal MO is matched to that of the $C_{alkane}2sp^3$ HO, the component energies and the total energy E_T of the $H-H$ bond are given by Eqs. (13.67-13.73) except that V_e, T, and V_m are corrected for the hybridization-energy-matching factor of 0.86359. Hybridization with 25% electron donation to the $C-C$-bond gives rise to the $C_{alkane}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{alkane},2sp^3\right)$ given by Eq. (14.515). The corresponding normalization factor for determining the zero of the total $H-H$ bond energy is given by the ratio of 15.75493 eV, the magnitude of $E_{Coulomb}\left(C_{alkane},2sp^3\right)$ given by Eq. (14.515), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). The hybridization energy factor $C_{alkaneC2sp^3HO}$ is

$$C_{alkaneC2sp^3HO}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{alkane2sp^3}}}=\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 0.86359 a_0}}=\frac{13.605804\ eV}{15.75493\ eV}=0.86359 \qquad (14.560)$$

Substitution of Eq. (14.558) into Eq. (13.233) with the hybridization factor of 0.86359 gives

$$0=\left[\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2}}}\left[(0.86359)^{-1}\left(\frac{3}{2}-\frac{3}{8}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2}}}{a-\sqrt{\frac{aa_0}{2}}}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{0.75e^2}{4\pi\varepsilon_o a^3}}\frac{m_e}{}}{m_e c^2}}\right]\right.$$
$$\left.+\hbar\sqrt{\frac{\frac{0.75e^2}{8\pi\varepsilon_o a^3}-\frac{e^2}{8\pi\varepsilon_o\left(a+c'\right)^3}}{0.5m_p}}\right] \qquad (14.561)$$

From the energy relationship given by Eq. (14.561) and the relationship between the axes given by Eqs. (14.558-14.559) and (14.62-14.63), the dimensions of the $H-H$ MO can be solved.

The most convenient way to solve Eq. (14.561) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a=5.8660a_0=3.1042\ X\ 10^{-10}\ m \qquad (14.562)$$

Substitution of Eq. (14.562) into Eq. (14.558) gives

$$c'=1.7126a_0=9.0627\ X\ 10^{-11}\ m \qquad (14.563)$$

The internuclear distance given by multiplying Eq. (14.563) by two is

$$2c' = 3.4252a_0 = 1.8125\,X\,10^{-10}\ m \tag{14.564}$$

Substitution of Eqs. (14.562-14.563) into Eq. (14.62) gives

$$b = c = 5.6104a_0 = 2.9689\,X\,10^{-10}\ m \tag{14.565}$$

Substitution of Eqs. (14.562-14.563) into Eq. (14.63) gives

$$e = 0.2920 \tag{14.566}$$

Using $2c'_{H-H}$ (Eq. (14.564)), the distance between the two H atoms when the total energy of the corresponding MO is zero (Eq. (14.561)), and $2c'_{C-H}$, the internuclear distance of each $C-H$ bond, the corresponding bond angle can be determined from the law of cosines. Since the internuclear distance of each $C-H$ bond of CH_3 (Eq. (14.545)) and CH_2 (Eq. (14.597)) are sufficiently equivalent, the bond angle determined with either is within experimental error of being the same. Using, Eqs. (13.242), (14.545), and (14.564), the bond angle θ between the $C-H$ bonds is

$$\theta = \cos^{-1}\left(\frac{2(2.09711)^2 - (3.4252)^2}{2(2.09711)^2}\right) = \cos^{-1}(-0.33383) = 109.50^\circ \tag{14.567}$$

The experimental angle between the $C-H$ bonds is [19]

$$\theta = 109.3^\circ \tag{14.568}$$

The CH_3 radical has a pyramidal structure with the carbon atom along the z-axis at the apex and the hydrogen atoms at the base in the xy-plane. The distance $d_{origin-H}$ from the origin to the nucleus of a hydrogen atom given by Eqs. (14.564) and (13.412) is

$$d_{origin-H} = 1.97754a_0 \tag{14.569}$$

The height along the z-axis of the pyramid from the origin to C nucleus d_{height} given by Eqs. (13.414), (14.545), and (14.569) is

$$d_{height} = 0.69800a_0 \tag{14.570}$$

The angle θ_v of each $C-H$ bond from the z-axis given by Eqs. (13.416), (14.569), and (14.570) is

$$\theta_v = 70.56^\circ \tag{14.571}$$

The $C-C$ bond is along the z-axis. Thus, the bond angle θ_{C-C-H} between the internuclear axis of the $C-C$ bond and a H atom of the methyl groups is given by

$$\theta_{C-C-H} = 180 - \theta_v \tag{14.572}$$

Substitution of Eq. (14.571) into Eq. (14.572) gives

$$\theta_{C-C-H} = 109.44° \tag{14.573}$$

The experimental angle between the $C-C-H$ bonds is [19]

$$\theta_{C-C-H} = 109.3° \tag{14.574}$$

The C_nH_{2n+2} MOs shown in Figures 50-60 were rendered using these parameters. A minimum energy is obtained with a staggered configuration consistent with observations [3].

ENERGIES OF THE CH_3 GROUPS

The energies of each CH_3 group of C_nH_{2n+2} are given by the substitution of the semiprincipal axes (Eqs. (14.543-14.544) and (14.547)) into the energy equations of methyl radical (Eqs. (13.556-13.560)), with the exception that $E\left(C_{alkane}, 2sp^3\right)$ (Eq. (14.514)) replaces $E\left(C, 2sp^3\right)$ in Eq. (13.560):

$$V_e = 3(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -107.32728\ eV \tag{14.575}$$

$$V_p = \frac{3e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 38.92728\ eV \tag{14.576}$$

$$T = 3(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 32.53914\ eV \tag{14.577}$$

$$V_m = 3(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.26957\ eV \tag{14.578}$$

$$E_{T_{alkane}}(CH_3) = \begin{pmatrix} -\frac{3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \\ -15.56407\ eV \end{pmatrix} = -67.69451\ eV \tag{14.579}$$

where $E_{T_{alkane}}(CH_3)$ is given by Eq. (14.540) which is reiteratively matched to Eq. (13.542) within five-significant-figure round off error.

VIBRATION OF THE $^{12}CH_3$ GROUPS

The vibrational energy levels of the $C-H$ bonds of CH_3 in C_nH_{2n+2} may be solved as three equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived

from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $^{12}CH_3$ GROUPS

The equations of the radiation reaction force of the methyl groups in C_nH_{2n+2} are the same as those of the methyl radical with the substitution of the methyl-group parameters. Using Eq. (13.561), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.49286\,X\,10^{16}\ rad/s \tag{14.580}$$

where b is given by Eq. (14.547). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.49286\,X\,10^{16}\ rad/s = 16.40846\ eV \tag{14.581}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.581) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(16.40846\ eV)}{m_e c^2}} = -0.25352\ eV \tag{14.582}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH_3 due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.582) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having three independent bonds, $\overline{E}'_{alkane\ osc}(^{12}CH_3)$ per bond is

$$\overline{E}'_{alkane\ osc}(^{12}CH_3) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.583}$$

$$\overline{E}'_{alkane\ osc}(^{12}CH_3) = -0.25352\ eV + \frac{1}{2}(0.35532\ eV) = -0.07586\ eV \tag{14.584}$$

Given that the vibration and reentrant oscillation is for three $C-H$ bonds, $\overline{E}_{alkane\ osc}\left({}^{12}CH_3\right)$, is:

$$\begin{aligned}\overline{E}_{alkane\ osc}\left({}^{12}CH_3\right) &= 3\left(\overline{E}_D+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= 3\left(-0.25352\ eV+\frac{1}{2}(0.35532\ eV)\right)\\ &= -0.22757\ eV\end{aligned} \tag{14.585}$$

5 TOTAL BOND ENERGIES OF THE ${}^{12}CH_3$ GROUPS

$E_{alkaneT+osc}\left({}^{12}CH_3\right)$, the total energy of each ${}^{12}CH_3$ group including the Doppler term, is given by the sum of $E_{T_{alkane}}\left(CH_3\right)$ (Eq. (14.579)) and $\overline{E}_{alkane\ osc}\left({}^{12}CH_3\right)$ given by Eq. (14.585):

$$\begin{aligned}E_{alkaneT+osc}\left(CH_3\right) &= V_e+T+V_m+V_p+E\left(C_{alkane},2sp^3\right)+\overline{E}_{alkane\ osc}\left({}^{12}CH_3\right)\\ &= E_{T_{alkane}}\left(CH_3\right)+\overline{E}_{alkane\ osc}\left({}^{12}CH_3\right)\end{aligned} \tag{14.586}$$

$$\begin{aligned}E_{alkaneT+osc}\left({}^{12}CH_3\right) &= \left\{\begin{array}{l}\left(\frac{-3e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV\right)\\ -3\left((31.63536831\ eV)\sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}}{m_e c^2}}-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{array}\right\}\\ &= -67.69450\ eV-3\left(0.25352\ eV-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned}$$

(14.587)

From Eqs. (14.585-14.587), the total energy of each ${}^{12}CH_3$ is

$$\begin{aligned}E_{alkaneT+osc}\left({}^{12}CH_3\right) &= -67.69450\ eV+\overline{E}_{alkane\ osc}\left({}^{12}CH_3\right)\\ &= -67.69450\ eV-3\left(0.25352\ eV-\frac{1}{2}(0.35532\ eV)\right)\\ &= -67.92207\ eV\end{aligned} \tag{14.588}$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The total CH_3 bond dissociation energy, $E_{D_{alkane}}\left(^{12}CH_3\right)$ is given by the sum of the initial $C2sp^3$ HO energy, $E\left(C,2sp^3\right)$ (Eq. (14.146)), and three times the energy of the hydrogen atom, $E_D(H)$ (Eq. (13.154)), minus $E_{alkaneT+osc}\left(^{12}CH_3\right)$ (Eq. (14.588)):

$$E_{D_{alkane}}\left(^{12}CH_3\right)=E\left(C,2sp^3\right)+3E(H)-E_{alkaneT+osc}\left(^{12}CH_3\right) \tag{14.589}$$

Thus, the total $^{12}CH_3$ bond dissociation energy, $E_{D_{alkane}}\left(^{12}CH_3\right)$ is

$$\begin{aligned}E_{D_{alkane}}\left(^{12}CH_3\right)&=-\left(14.63489\ eV+3\left(13.59844\ eV\right)\right)-\left(E_{alkaneT+osc}\left(^{12}CH_2\right)\right)\\&=-55.43021\ eV-\left(-67.92207\ eV\right)\\&=12.49186\ eV\end{aligned} \tag{14.590}$$

FORCE BALANCE OF THE CH_2 MOs OF CONTINUOUS-CHAIN ALKANES

Each of the CH_2 MOs must comprise two equivalent $C-H$ bonds with each comprising 75% of a H_2-type ellipsoidal MO and a $C2sp^3$ HO as given by Eq. (13.494):

$$2\left[1\ C2sp^3+0.75\ H_2\ MO\right]\rightarrow CH_2\ MO \tag{14.591}$$

The force balance of each CH_2 MO is determined by the boundary conditions that arise from the linear combination of orbitals according to Eq. (14.591) and the energy matching condition between the hydrogen and $C2sp^3$ HO components of the MO.

The force constant k' to determine the ellipsoidal parameter c' of the each H_2-type-ellipsoidal-MO component of the CH_2 MO in terms of the central force of the foci is given by Eq. (13.59). The distance from the origin of each $C-H$-bond MO to each focus c' is given by Eq. (13.60). The internuclear distance is given by Eq. (13.61). The length of the semiminor axis of the prolate spheroidal $C-H$-bond MO $b=c$ is given by Eq. (13.62). The eccentricity, e, is given by Eq. (13.63). The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each $C-H$-bond MO. Since each of the two prolate spheroidal $C-H$-bond MOs comprises an H_2-type-ellipsoidal MO that transitions to the $C_{alkane}2sp^3$ HO of C_nH_{2n+2}, the energy $E\left(C_{alkane},2sp^3\right)$

of Eq. (14.512) adds to that of the two corresponding H_2-type ellipsoidal MOs to give the total energy of the CH_2 MO. From the energy equation and the relationship between the axes, the dimensions of the CH_2 MO are solved.

The energy components of V_e, V_p, T, and V_m are the same as those of dihydrogen carbide radical, two times those of CH corresponding to the two $C-H$ bonds except that energy of the $C_{alkane}2sp^3$ HO is used. Since the each prolate spheroidal H_2-type MO transitions to the $C_{alkane}2sp^3$ HO and the energy of the $C_{alkane}2sp^3$ shell treated independently must remain constant and equal to the $E\left(C_{alkane},2sp^3\right)$ given by Eq. (14.512), the total energy $E_{T_{alkane}}\left(CH_2\right)$ of the CH_2 MO is given by the sum of the energies of the orbitals corresponding to the composition of the linear combination of the $C_{alkane}2sp^3$ HO and the two H_2-type ellipsoidal MOs that forms the CH_2 MO as given by Eq. (14.591). Using Eq. (13.431) or Eq. (13.495), $E_{T_{alkane}}\left(CH_2\right)$ is given by

$$\begin{aligned} E_{T_{alkane}}\left(CH_2\right) &= E_T + E\left(C_{alkane},2sp^3\right) \\ &= -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV \end{aligned} \tag{14.592}$$

$E_{T_{alkane}}\left(CH_2\right)$ given by Eq. (14.592) is set equal to two times the energy of the H_2-type ellipsoidal MO minus the Coulombic energy of H given by Eq. (13.496):

$$E_T\left(CH_2\right) = -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV = -49.66493\ eV \tag{14.593}$$

From the energy relationship given by Eq. (14.593) and the relationship between the axes given by Eqs. (13.60-13.63), the dimensions of the CH_2 MO can be solved.

Substitution of Eq. (13.60) into Eq. (14.593) gives

$$\frac{2e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}}-1\right] = e34.10086 \tag{14.594}$$

The most convenient way to solve Eq. (14.594) is by the reiterative technique using a computer. The result to within the round-off error with five-significant figures is

$$a = 1.67122a_0 = 8.84370\ X\ 10^{-11}\ m \tag{14.595}$$

Substitution of Eq. (14.595) into Eq. (14.60) gives

$$c' = 1.05553a_0 = 5.58563\ X\ 10^{-11}\ m \tag{14.596}$$

The internuclear distance given by multiplying Eq. (14.596) by two is

$$2c' = 2.11106a_0 = 1.11713\ X\ 10^{-10}\ m \tag{14.597}$$

The experimental $C-H$ bond distance of butane is [3]

$$2c' = 1.117\ X\ 10^{-10}\ m \tag{14.598}$$

Substitution of Eqs. (14.595-14.596) into Eq. (14.62) gives

$$b = c = 1.29569a_0 = 6.85652\ X\ 10^{-11}\ m \tag{14.599}$$

Substitution of Eqs. (14.595-14.596) into Eq. (14.63) gives

$$e = 0.63159 \tag{14.600}$$

The nucleus of the H atom and the nucleus of the C atom comprise the foci of each H_2-type ellipsoidal MO. The parameters of the point of intersection of the H_2-type ellipsoidal MO and the $C_{alkane}2sp^3$ HO are given by Eqs. (13.84-13.95) and (13.261-13.270). The polar intersection angle θ' is given by Eq. (13.261) where $r_n = r_{methylene\,2sp^3} = 0.81549a_0$ is the radius of the $C_{methylene}2sp^3$ shell (Eq. (14.521)). Substitution of Eqs. (14.595-14.596) into Eq. (13.261) gives

$$\theta' = 68.47° \tag{14.601}$$

Then, the angle $\theta_{C-H_{alkane}\,2sp^3HO}$ the radial vector of the $C2sp^3$ HO makes with the internuclear axis is

$$\theta_{C-H_{alkane}\,2sp^3HO} = 180° - 68.47° = 111.53° \tag{14.602}$$

as shown in Figure 49. The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals. Thus, the angle $\omega t = \theta_{C-H_{alkane},H_2MO}$ between the internuclear axis and the point of intersection of the H_2-type ellipsoidal MO with the $C_{alkane}2sp^3$ radial vector obeys the following relationship:

$$r_{alkane\,2sp^3}\sin\theta_{C-H_{alkane}\,2sp^3HO} = 0.81549a_0\sin\theta_{C-H_{alkane}\,2sp^3HO} = b\sin\theta_{C-H_{alkane},H_2MO} \tag{14.603}$$

such that

$$\theta_{C-H_{alkane},H_2MO} = \sin^{-1}\frac{0.81549a_0\sin\theta_{C-H_{alkane}\,2sp^3HO}}{b} = \sin^{-1}\frac{0.81549a_0\sin 111.53°}{b} \tag{14.604}$$

with the use of Eq. (14.602). Substitution of Eq. (14.599) into Eq. (14.604) gives

$$\theta_{C-H_{alkane},H_2MO} = 35.84° \tag{14.605}$$

Then, the distance d_{C-H_{alkane},H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane},H_2MO} = a\cos\theta_{C-H_{alkane},H_2MO} \tag{14.606}$$

Substitution of Eqs. (14.595) and (14.605) into Eq. (14.606) gives

$$d_{C-H_{alkane},H_2MO} = 1.35486a_0 = 7.16963\,X\,10^{-11}\,m \tag{14.607}$$

The distance $d_{C-H_{alkane}2sp^3HO}$ along the internuclear axis from the origin of the C atom to the point of intersection of the orbitals is given by

$$d_{C-H_{alkane}2sp^3HO} = d_{C-H_{alkane},H_2MO} - c' \tag{14.608}$$

Substitution of Eqs. (14.596) and (14.605) into Eq. (14.608) gives

$$d_{C-H_{alkane}2sp^3HO} = 0.29933a_0 = 1.58400\,X\,10^{-11}\,m \tag{14.609}$$

The charge-density in each $C-C$-bond MO is increased by a factor of 0.25 with the formation of the $C_{alkane}2sp^3$ HOs each having a smaller radius. Using the orbital composition of the $C-C$-bond MOs (Eq. (14.504), CH_3 groups (Eq. (14.539)), and the CH_2 groups (Eq. (14.591)), the radii of $C1s = 0.17113a_0$ (Eq. (10.51)), $C_{alkane}2sp^3 = 0.86359a_0$ (Eq. (14.514)), and $C_{alkane}2sp^3 = C_{methylene}2sp^3 = 0.81549a_0$ (Eq. (14.521)) shells, the parameters of the $C-C$-bonds (Eqs. (13.3-13.4), (14.523-14.525), and (14.528-14.538)), the parameters of the $C-H$-bond MOs of the CH_3 groups (Eqs. (13.3-13.4), (14.544-14.545), and (14.547-14.557)), the parameters of the $C-H$-bond MOs of the CH_2 groups (Eqs. (13.3-13.4), (14.595-14.597), and (14.599-14.609)), and the bond-angle parameters (Eqs. (14.562-14.574)), the charge-density of the C_nH_{2n+2} MO comprising the linear combination $2n+2$ $C-H$-bond MOs and $n-1$ $C-C$-bond MOs, each bridging one or more methyl or methylene groups is shown for representative cases where data was available [17-18]. Propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane are shown in Figures 50-60, respectively. Each $C-H$-bond MO comprises a H_2-type ellipsoidal MO and a $C_{alkane}2sp^3$ HO having the dimensional diagram shown in Figure 48. Each $C-C$-bond MO comprises a H_2-type ellipsoidal MO bridging two $C_{alkane}2sp^3$ HOs having the dimensional diagram shown in Figure 49.

ENERGIES OF THE CH_2 GROUPS

The energies of each CH_2 group of C_nH_{2n+2} are given by the substitution of the semiprincipal axes (Eqs. (14.595-14.596) and (14.599)) into the energy equations of dihydrogen carbide radical (Eqs. (13.510-13.514)), with the exception that $E\left(C_{alkane}, 2sp^3\right)$ (Eq. (14.512)) replaces $E\left(C, 2sp^3\right)$ in Eq. (13.514):

$$V_e = 2(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -70.41425\ eV \tag{14.610}$$

$$V_p = \frac{2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}} = 25.78002\ eV \tag{14.611}$$

$$T = 2(0.91771)\frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 21.06675\ eV \tag{14.612}$$

$$V_m = 2(0.91771)\frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -10.53337\ eV \tag{14.613}$$

$$E_{T_{alkane}}(CH_2) = -\frac{2e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV = -49.66493\ eV \tag{14.614}$$

where $E_{T_{alkane}}(CH_2)$ is given by Eq. (14.592) which is reiteratively matched to Eq. (13.496) within five-significant-figure round off error.

VIBRATION OF THE $^{12}CH_2$ GROUPS

The vibrational energy levels of the $C-H$ bonds of CH_2 in C_nH_{2n+2} may be solved as two equivalent coupled harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $^{12}CH_2$ GROUPS

The equations of the radiation reaction force of the methylene groups in C_nH_{2n+2} are the same as those of the dihydrogen carbide radical with the substitution of the methylene-group

parameters. Using Eq. (13.515), the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{\frac{0.75e^2}{4\pi\varepsilon_0 b^3}}{m_e}} = 2.42751\ X\ 10^{16}\ rad/s \tag{14.615}$$

where b is given by Eq. (14.599). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 2.42751\ X\ 10^{16}\ rad/s = 15.97831\ eV \tag{14.616}$$

In Eq. (11.181), substitution of $E_T(H_2)$ (Eqs. (11.212) and (13.75)), the maximum total energy of each H_2-type MO, for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.616) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the three bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -31.63537\ eV\sqrt{\frac{2e(15.97831\ eV)}{m_e c^2}} = -0.25017\ eV \tag{14.617}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of CH_2 due to the reentrant orbit of each bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.617) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-H$ bond. Using ω_e given by Eq. (13.458) for $\overline{E}_{Kvib}$ of the transition state having two independent bonds, $\overline{E}'_{alkane\ osc}\left({}^{12}CH_2\right)$ per bond is

$$\overline{E}'_{alkane\ osc}\left({}^{12}CH_2\right) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.618}$$

$$\overline{E}'_{alkane\ osc}\left({}^{12}CH_2\right) = -0.25017\ eV + \frac{1}{2}(0.35532\ eV) = -0.07251\ eV \tag{14.619}$$

Given that the vibration and reentrant oscillation is for two $C-H$ bonds, $\overline{E}_{alkane\ osc}\left({}^{12}CH_2\right)$, is:

$$\overline{E}_{alkane\ osc}\left({}^{12}CH_2\right) = 2\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) = 2\left(-0.25017\ eV + \frac{1}{2}(0.35532\ eV)\right) = -0.14502\ eV$$

(14.620)

TOTAL BOND ENERGIES OF THE $^{12}CH_2$ GROUPS

$E_{alkaneT+osc}\left(^{12}CH_2\right)$, the total energy of each $^{12}CH_2$ group including the Doppler term, is given by the sum of $E_{T_{alkane}}\left(CH_2\right)$ (Eq. (14.614)) and $\overline{E}_{alkane\ osc}\left(^{12}CH_2\right)$ given by Eq. (14.620):

$$\begin{aligned} E_{alkaneT+osc}\left(CH_2\right) &= V_e + T + V_m + V_p + E\left(C_{alkane}, 2sp^3\right) + \overline{E}_{alkane\ osc}\left(^{12}CH_2\right) \\ &= E_{T_{alkane}}\left(CH_2\right) + \overline{E}_{alkane\ osc}\left(^{12}CH_2\right) \end{aligned} \tag{14.621}$$

$$\begin{aligned} E_{alkaneT+osc}\left(^{12}CH_2\right) &= \left\{ \begin{array}{l} \left(\frac{-2e^2}{8\pi\varepsilon_0 c'} \left[(0.91771)\left(2 - \frac{1}{2}\frac{a_0}{a}\right) \ln\frac{a+c'}{a-c'} - 1 \right] - 15.56407\ eV \right) \\ -2\left((31.63536831\ eV) \sqrt{\frac{2\hbar\sqrt{\frac{3}{4}\frac{e^2}{4\pi\varepsilon_o b^3}}}{m_e c^2}} - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \end{array} \right\} \\ &= -49.66493\ eV - 2\left(0.25017\ eV - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \end{aligned}$$

(14.622)

From Eqs. (14.620-14.622), the total energy of each $^{12}CH_2$ is

$$\begin{aligned} E_{alkaneT+osc}\left(^{12}CH_2\right) &= -49.66493\ eV + \overline{E}_{alkane\ osc}\left(^{12}CH_2\right) \\ &= -49.66493\ eV - 2\left(0.25017\ eV - \frac{1}{2}(0.35532\ eV) \right) \\ &= -49.80996\ eV \end{aligned} \tag{14.623}$$

where ω_e given by Eq. (13.458) was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

The derivation of the total CH_2 bond dissociation energy, $E_{D_{alkane}}\left(^{12}CH_2\right)$ follows from that of the bond dissociation energy of dihydrogen carbide radical, $E_D\left(^{12}CH_2\right)$, given by Eqs. (13.524-13.527). $E_{D_{alkane}}\left(^{12}CH_2\right)$ is given by the sum of the initial $C2sp^3$ HO energy, $E\left(C, 2sp^3\right)$ (Eq. (14.146)), and two times the energy of the hydrogen atom, $E(H)$ (Eq. (13.154)), minus the sum of $E_{alkaneT+osc}\left(^{12}CH_2\right)$ (Eq. (14.623)) and $E(magnetic)$ (Eq. 13.524)):

$$E_{D_{alkane}}\left({}^{12}CH_2\right)=E\left(C,2sp^3\right)+2E(H)-E_{alkaneT+osc}\left({}^{12}CH_2\right)-E\left(magnetic\right) \quad (14.624)$$

Thus, the total ${}^{12}CH_2$ bond dissociation energy, $E_{D_{alkane}}\left({}^{12}CH_2\right)$ is

$$\begin{aligned}E_{D_{alkane}}\left({}^{12}CH_2\right)&=-\left(14.63489\ eV+2\left(13.59844\ eV\right)\right)-\left(E_{alkaneT+osc}\left({}^{12}CH_2\right)+E\left(magnetic\right)\right)\\&=-41.83177\ eV-\left(-49.80996\ eV+0.14803\ eV\right)\\&=7.83016\ eV\end{aligned} \quad (14.625)$$

SUM OF THE ENERGIES OF THE $C-C$ σ MOs AND THE HOs OF CONTINUOUS-CHAIN ALKANES

The energy components of V_e, V_p, T, V_m, and E_T of the $C-C$-bond MOs are the same as those of the CH MO except that energy of the $C_{alkane}2sp^3$ HO is used. The energies of each $C-C$-bond MO are given by the substitution of the semiprincipal axes (Eqs. (14.523-14.524) and (14.528)) into the energy equations of the CH MO (Eqs. (13.449-13.453)), with the exception that $E\left(C_{alkane},2sp^3\right)$ (Eq. (14.512)) replaces $E\left(C,2sp^3\right)$ in Eq. (13.453). The total number of $C-C$ bonds of C_nH_{2n+2} is $n-1$. Thus, the energies of the $n-1$ bonds is given by

$$V_e=(n-1)(0.91771)\frac{-2e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-(n-1)28.79214\ eV \quad (14.626)$$

$$V_p=\frac{(n-1)e^2}{8\pi\varepsilon_0\sqrt{a^2-b^2}}=(n-1)9.33352\ eV \quad (14.627)$$

$$T=(n-1)(0.91771)\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=(n-1)6.77464\ eV \quad (14.628)$$

$$V_m=(n-1)(0.91771)\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}=-(n-1)3.38732\ eV \quad (14.629)$$

$$\begin{aligned}E_{T_{alkane}}(C-C,\sigma)&=-\frac{(n-1)e^2}{8\pi\varepsilon_0c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]-15.56407\ eV\\&=-(n-1)31.63537\ eV\end{aligned} \quad (14.630)$$

where $E_{T_{alkane}}(C-C,\sigma)$ is the total energy of the $C-C$ σ MOs given by Eq. (14.520) which is reiteratively matched to Eq. (13.75) within five-significant-figure round off error.

Since there are two carbon atoms per bond, the number of $C-C$ bonds is $n-1$, and the energy change of each $C2sp^3$ shell due to the decrease in radius with the formation of each $C-C$-bond MO is $E_{T_{alkane}}\left(C-C,2sp^3\right)$ (Eq. (14.517)), the total energy of the $C-C$-bond MOs, $E_{T_{alkane}}\left(C-C\right)$, is given by the sum of $2(n-1)E_{T_{alkane}}\left(C-C,2sp^3\right)$ and $E_{T_{alkane}}\left(C-C,\sigma\right)$, the σ MO contribution given by Eq. (14.630):

$$\begin{aligned}E_{T_{alkane}}\left(C-C\right)&=2(n-1)E_{T_{alkane}}\left(C-C,2sp^3\right)+E_{T_{alkane}}\left(C-C,\sigma\right)\\&=(n-1)\left(\begin{array}{l}2(-0.92918\ eV)\\+\left(\begin{array}{l}-\dfrac{e^2}{8\pi\varepsilon_0\sqrt{aa_0}}\left[(0.91771)\left(2-\dfrac{1}{2}\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{aa_0}}{a-\sqrt{aa_0}}-1\right]\\-15.56407\ eV\end{array}\right)\end{array}\right)\\&=(n-1)\left(2(-0.92918\ eV)+(-31.63537\ eV)\right)\\&=-(n-1)33.49373\ eV\end{aligned}\qquad(14.631)$$

VIBRATION OF CONTINUOUS-CHAIN ALKANES

The vibrational energy levels of the $C-C$ bonds of C_nH_{2n+2} may be solved as $n-1$ sets of coupled carbon harmonic oscillators wherein each carbon is further coupled to two or three equivalent H harmonic oscillators by developing the Lagrangian, the differential equation of motion, and the eigenvalue solutions [9] wherein the spring constants are derived from the central forces as given in the Vibration of Hydrogen-Type Molecular Ions section and the Vibration of Hydrogen-Type Molecules section.

THE DOPPLER ENERGY TERMS OF THE $C-C$-BOND MOs OF CONTINUOUS-CHAIN ALKANES

The equations of the radiation reaction force of each symmetrical $C-C$-bond MO are given by Eqs. (11.231-11.233), except the force-constant factor is 0.5 based on the force constant k' of Eq. (14.152), and the $C-C$-bond MO parameters are used. The angular frequency of the reentrant oscillation in the transition state is

$$\omega=\sqrt{\frac{\dfrac{0.5e^2}{4\pi\varepsilon_0 a^3}}{m_e}}=9.43699\,X\,10^{15}\ rad/s\qquad(14.632)$$

where a is given by Eq. (14.523). The kinetic energy, E_K, is given by Planck's equation (Eq. (11.127)):

$$\overline{E}_K = \hbar\omega = \hbar 9.43699\, X\, 10^{15}\ rad/s = 6.21159\ eV \tag{14.633}$$

In Eq. (11.181), substitution of $E_{T_{alkane}}(C-C)$ (Eq. (14.631)) with $n=2$ for $E_{h\nu}$, the mass of the electron, m_e, for M, and the kinetic energy given by Eq. (14.633) for $\overline{E}_K$ gives the Doppler energy of the electrons of each of the bonds for the reentrant orbit:

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{Mc^2}} = -33.49373\ eV\sqrt{\frac{2e(6.21159\ eV)}{m_e c^2}} = -0.16515\ eV \tag{14.634}$$

In addition to the electrons, the nuclei also undergo simple harmonic oscillation in the transition state at their corresponding frequency. The decrease in the energy of each $C-C$-bond MO due to the reentrant orbit of the bond in the transition state corresponding to simple harmonic oscillation of the electrons and nuclei, $\overline{E}_{osc}$, is given by the sum of the corresponding energies, $\overline{E}_D$ given by Eq. (14.634) and $\overline{E}_{Kvib}$, the average kinetic energy of vibration which is 1/2 of the vibrational energy of each $C-C$ bond. Using the ethane experimental $C-C$ $E_{vib}(\upsilon_3)$ of 993 cm^{-1} $(0.12312\ eV)$ [10] for $\overline{E}_{Kvib}$ of the transition state having $n-1$ independent bonds, $\overline{E}'_{alkane\ osc}(C-C,\sigma)$ per bond is

$$\overline{E}'_{alkane\ osc}(C-C,\sigma) = \overline{E}_D + \overline{E}_{Kvib} = \overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \tag{14.635}$$

$$\overline{E}'_{alkane\ osc}(C-C,\sigma) = -0.16515\ eV + \frac{1}{2}(0.12312\ eV) = -0.10359\ eV \tag{14.636}$$

Given that the vibration and reentrant oscillation is for $n-1$ $C-C$ bonds, $\overline{E}_{alkane\ osc}(C-C,\sigma)$, is:

$$\begin{aligned}\overline{E}_{alkane\ osc}(C-C,\sigma) &= (n-1)\left(\overline{E}_D + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\\ &= (n-1)\left(-0.16515\ eV + \frac{1}{2}(0.12312\ eV)\right)\\ &= -(n-1)0.10359\ eV\end{aligned} \tag{14.637}$$

TOTAL ENERGIES OF THE $C-C$-BOND MOs OF CONTINUOUS-CHAIN ALKANES

$E_{alkaneT+osc}(C-C)$, the total energy of the $n-1$ bonds of the $C-C$-bond MOs including the Doppler term, is given by the sum of $E_{T_{alkane}}(C-C)$ (Eq. (14.631)) and $\overline{E}_{alkane\ osc}(C-C,\sigma)$ given by Eq. (14.637):

$$\begin{aligned}E_{alkaneT+osc}(C-C)&=\left((n-1)\begin{pmatrix}V_e+T+V_m+V_p+E\left(C_{alkane},2sp^3\right)\\+2E_{T_{alkane}}\left(C-C,2sp^3\right)\end{pmatrix}+\overline{E}_{alkane\ osc}(C-C,\sigma)\right)\\&=E_{T_{alkane}}(C-C,\sigma)+2(n-1)E_{T_{alkane}}\left(C-C,2sp^3\right)+\overline{E}_{alkane\ osc}(C-C,\sigma)\\&=E_{T_{alkane}}(C-C)+\overline{E}_{alkane\ osc}(C-C,\sigma)\end{aligned} \tag{14.638}$$

$$\begin{aligned}E_{alkaneT+osc}(C-C)&=(n-1)\left\{\begin{pmatrix}\frac{-e^2}{8\pi\varepsilon_0 c'}\left[(0.91771)\left(2-\frac{1}{2}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\\-15.56407\ eV+2E_{T_{alkane}}\left(C-C,2sp^3\right)\end{pmatrix}\right.\\&\left.\begin{pmatrix}1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{1}{2}\frac{e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}}\end{pmatrix}+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}\\&=(n-1)\left(-33.49373\ eV-0.16515\ eV+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)\end{aligned} \tag{14.639}$$

From Eqs. (14.637-14.639), the total energy of the $n-1$ bonds of the $C-C$-bond MOs is

$$\begin{aligned}E_{alkaneT+osc}(C-C)&=(n-1)\left(-31.63537\ eV+2E_{T_{alkane}}\left(C-C,2sp^3\right)\right)+\overline{E}_{alkane\ osc}(C-C,\sigma)\\&=(n-1)\begin{pmatrix}-31.63537\ eV+2(-0.92918\ eV)\\-0.16515\ eV+\frac{1}{2}(0.12312\ eV)\end{pmatrix}\\&=-(n-1)33.59732\ eV\end{aligned} \tag{14.640}$$

where the experimental E_{vib} was used for the $\hbar\sqrt{\frac{k}{\mu}}$ term.

TOTAL BOND ENERGY OF THE $C-C$ BONDS OF CONTINUOUS-CHAIN ALKANES

Since there are two carbon atoms per bond and the number of $C-C$ bonds is $n-1$, the total bond energy of the $C-C$ bonds of C_nH_{2n+2}, $E_D(C-C)_{n-1}$, is given by $2(n-1)E(C,2sp^3)$ minus $E_{alkaneT+osc}(C-C)$ (Eq. (14.640)) where $E(C,2sp^3)$ (Eq. (14.146)) is the initial energy of each $C2sp^3$ HO of the CH_3 and CH_2 groups that bond to the $C-C$ bonds. Thus, the total dissociation energy of the $C-C$ bonds of C_nH_{2n+2}, is

$$\begin{aligned} E_D(C-C)_{n-1} &= 2(n-1)\left(E(C,2sp^3)\right)-\left(E_{alakneT+osc}(C-C)\right) \\ &= 2(n-1)(-14.63489\ eV)-(n-1)(-33.59732\ eV) \\ &= (n-1)(2(-14.63489\ eV)-(-33.59732\ eV)) \\ &= (n-1)(4.32754\ eV) \end{aligned} \tag{14.641}$$

TOTAL ENERGY OF CONTINUOUS-CHAIN ALKANES

$E_D(C_nH_{2n+2})$, the total bond dissociation energy of C_nH_{2n+2}, is given as the sum of the energy components due to the two methyl groups, $n-2$ methylene groups, and $n-1$ $C-C$ bonds where each energy component is given by Eqs. (14.590), (14.625), and (14.641), respectively. Thus, the total bond dissociation energy of C_nH_{2n+2} is

$$\begin{aligned} E_D(C_nH_{2n+2}) &= E_D(C-C)_{n-1}+2E_{D_{alkane}}\left({}^{12}CH_3\right)+(n-2)E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (n-1)(4.32754\ eV)+2(12.49186\ eV)+(n-2)(7.83016\ eV) \end{aligned} \tag{14.642}$$

The experimental total bond dissociation energy of C_nH_{2n+2}, $E_{D_{exp}}(C_nH_{2n+2})$, is given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_nH_{2n+2}(gas))$) and the sum of the enthalpy of the formation of the reactant gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms:

$$\begin{aligned} E_{D_{exp}}(C_nH_{2n+2}) &= -\left\{\Delta H_f(C_nH_{2n+2}(gas))-\left[n\Delta H_f(C(gas))+(2n+2)\Delta H_f(H(gas))\right]\right\} \\ &= -\left\{\Delta H_f(C_nH_{2n+2}(gas))-\left[n7.42774\ eV+(2n+2)2.259353\ eV\right]\right\} \end{aligned} \tag{14.643}$$

where the heats of formation atomic carbon and hydrogen gas are given by [17-18]

$$\Delta H_f(C(gas)) = 716.68\ kJ/mole\ (7.42774\ eV/molecule) \tag{14.644}$$

$$\Delta H_f(H(gas)) = 217.998\ kJ/mole\ (2.259353\ eV/molecule) \tag{14.645}$$

Using the corresponding experimental $\Delta H_f\left(C_nH_{2n+2}(gas)\right)$ [18], $E_D\left(C_nH_{2n+2}\right)$ was determined from propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane in the corresponding sections, and the results of the determination of the total energies are given in Table 14.1. The calculated results are based on first principles and given in closed-form, exact equations containing fundamental constants only. The agreement between the experimental and calculated results is excellent.

Using the results for C_nH_{2n+2} and the functional groups as basis sets that are linearly combined, the exact solution for the dimensional parameters, charge density functions, and energies of all molecules can be obtained. For example, one or more of the hydrogen atoms of the solution for C_nH_{2n+2} can be substituted with one or more of the previously solved functional groups or derivative functional groups to give a desired molecule. The solution is given by energy matching each group to C_nH_{2n+2}. Substitution of one or more H's of C_nH_{2n+2} with functional groups from the list of CH_3, other C_nH_{2n+2} groups, $H_2C=CH_2$, $HC\equiv CH$, F, Cl, O, OH, NH, NH_2, CN, NO, NO_2, CO, CO_2, and C_6H_6 give the solutions of branched alkanes, alkenes, and alkynes, alkyl halides, ethers, alcohols, amides, amines, nitriles, alkyl nitrosos, alkyl nitrates, aldehydes, ketones, carbolylic acids, esters, and substituted aromatics.

PROPANE (C_3H_8)

Using Eq. (14.642) with $n=3$, the total bond dissociation energy of C_3H_8 is

$$\begin{aligned} E_D\left(C_3H_8\right) &= E_D\left(C-C\right)_2+2E_{D_{alkane}}\left({}^{12}CH_3\right)+E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (2)(4.32754\ eV)+(2)(12.49186\ eV)+(1)(7.83016\ eV) \\ &= 41.46896\ eV \end{aligned} \tag{14.646}$$

Using Eq. (14.643), the experimental total bond dissociation energy of C_3H_8, $E_{D_{\exp}}\left(C_3H_8\right)$, given by the negative difference between the enthalpy of its formation ($\Delta H_f\left(C_3H_8(gas)=-1.0758\ eV\right)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f\left(C(gas)\right)$) and hydrogen ($\Delta H_f\left(H(gas)\right)$) atoms is

$$\begin{aligned} E_{D_{\exp}}\left(C_3H_8\right) &= -\left\{\Delta H_f\left(C_3H_8(gas)\right)-\left[3\Delta H_f\left(C(gas)\right)+8\Delta H_f\left(H(gas)\right)\right]\right\} \\ &= -\left\{-1.0758\ eV-\left[(3)7.42774\ eV+(8)2.259353\ eV\right]\right\} \\ &= 41.434\ eV \end{aligned} \tag{14.647}$$

The charge-density of the C_3H_8 molecular orbital (MO) comprising a linear combination of two methyl groups and one methylene group is shown in Figure 50.

BUTANE (C_4H_{10})

Using Eq. (14.642) with $n=4$, the total bond dissociation energy of C_4H_{10} is

$$\begin{aligned} E_D(C_4H_{10}) &= E_D(C-C)_3 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 2E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (3)(4.32754\ eV) + (2)(12.49186\ eV) + (2)(7.83016\ eV) \\ &= 53.62666\ eV \end{aligned} \tag{14.648}$$

Using Eq. (14.643), the experimental total bond dissociation energy of C_4H_{10}, $E_{D_{\exp}}(C_4H_{10})$, given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_4H_{10}(gas) = -1.3028\ eV)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms is

$$\begin{aligned} E_{D_{\exp}}(C_4H_{10}) &= -\left\{\Delta H_f(C_4H_{10}(gas)) - \left[4\Delta H_f(C(gas)) + 10\Delta H_f(H(gas))\right]\right\} \\ &= -\left\{-1.3028\ eV - \left[(4)7.42774\ eV + (10)2.259353\ eV\right]\right\} \\ &= 53.61\ eV \end{aligned} \tag{14.649}$$

The charge-density of the C_4H_{10} molecular orbital (MO) comprising a linear combination of two methyl and two methylene groups is shown in Figure 51.

PENTANE (C_5H_{12})

Using Eq. (14.642) with $n=5$, the total bond dissociation energy of C_5H_{12} is

$$\begin{aligned} E_D(C_5H_{12}) &= E_D(C-C)_4 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 3E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (4)(4.32754\ eV) + (2)(12.49186\ eV) + (3)(7.83016\ eV) \\ &= 65.78436\ eV \end{aligned} \tag{14.650}$$

Using Eq. (14.643), the experimental total bond dissociation energy of C_5H_{12}, $E_{D_{\exp}}(C_5H_{12})$, given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_5H_{12}(gas) = -1.5225\ eV)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms is

$$E_{D_{exp}}(C_5H_{12}) = -\left\{\Delta H_f(C_5H_{12}(gas)) - \left[5\Delta H_f(C(gas)) + 12\Delta H_f(H(gas))\right]\right\}$$
$$= -\left\{-1.5225\ eV - \left[(5)7.42774\ eV + (12)2.259353\ eV\right]\right\} \quad (14.651)$$
$$= 65.77\ eV$$

The charge-density of the C_5H_{12} molecular orbital (MO) comprising a linear combination of two methyl and three methylene groups is shown in Figure 52.

HEXANE (C_6H_{14})

Using Eq. (14.642) with $n = 6$, the total bond dissociation energy of C_6H_{14} is

$$E_D(C_6H_{14}) = E_D(C-C)_5 + 2E_{D_{alkane}}(^{12}CH_3) + 4E_{D_{alkane}}(^{12}CH_2)$$
$$= (5)(4.32754\ eV) + (2)(12.49186\ eV) + (4)(7.83016\ eV) \quad (14.652)$$
$$= 77.94206\ eV$$

Using Eq. (14.643), the experimental total bond dissociation energy of C_6H_{14}, $E_{D_{exp}}(C_6H_{14})$, given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_6H_{14}(gas) = -1.7298\ eV)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms is

$$E_{D_{exp}}(C_6H_{14}) = -\left\{\Delta H_f(C_6H_{14}(gas)) - \left[6\Delta H_f(C(gas)) + 14\Delta H_f(H(gas))\right]\right\}$$
$$= -\left\{-1.7298\ eV - \left[(6)7.42774\ eV + (14)2.259353\ eV\right]\right\}$$
$$= 77.93\ eV$$

(14.653)

The charge-density of the C_6H_{14} molecular orbital (MO) comprising a linear combination of two methyl and four methylene groups is shown in Figure 53.

HEPTANE (C_7H_{16})

Using Eq. (14.642) with $n = 7$, the total bond dissociation energy of C_7H_{16} is

$$E_D(C_7H_{16}) = E_D(C-C)_6 + 2E_{D_{alkane}}(^{12}CH_3) + 5E_{D_{alkane}}(^{12}CH_2)$$
$$= (6)(4.32754\ eV) + (2)(12.49186\ eV) + (5)(7.83016\ eV) \quad (14.654)$$
$$= 90.09976\ eV$$

Using Eq. (14.643), the experimental total bond dissociation energy of C_7H_{16}, $E_{D_{exp}}(C_7H_{16})$, given by the negative difference between the enthalpy of its formation

$(\Delta H_f(C_7H_{16}(gas) = -1.9443\ eV))$ [18] and the sum of the enthalpy of the formation of the gaseous carbons $(\Delta H_f(C(gas)))$ and hydrogen $(\Delta H_f(H(gas)))$ atoms is

$$\begin{aligned} E_{D_{exp}}(C_7H_{16}) &= -\left\{\Delta H_f(C_7H_{16}(gas)) - \left[7\Delta H_f(C(gas)) + 16\Delta H_f(H(gas))\right]\right\} \\ &= -\left\{-1.9443\ eV - \left[(7)7.42774\ eV + (16)2.259353\ eV\right]\right\} \\ &= 90.09\ eV \end{aligned} \tag{14.655}$$

The charge-density of the C_7H_{16} MO comprising a linear combination of two methyl and five methylene groups is shown in Figure 54.

OCTANE (C_8H_{18})

Using Eq. (14.642) with $n = 8$, the total bond dissociation energy of C_8H_{18} is

$$\begin{aligned} E_D(C_8H_{18}) &= E_D(C-C)_7 + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 6E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (7)(4.32754\ eV) + (2)(12.49186\ eV) + (6)(7.83016\ eV) \\ &= 102.25746\ eV \end{aligned} \tag{14.656}$$

Using Eq. (14.643), the experimental total bond dissociation energy of C_8H_{18}, $E_{D_{exp}}(C_8H_{18})$, given by the negative difference between the enthalpy of its formation $(\Delta H_f(C_8H_{18}(gas) = -2.1609\ eV))$ [18] and the sum of the enthalpy of the formation of the gaseous carbons $(\Delta H_f(C(gas)))$ and hydrogen $(\Delta H_f(H(gas)))$ atoms is

$$\begin{aligned} E_{D_{exp}}(C_8H_{18}) &= -\left\{\Delta H_f(C_8H_{18}(gas)) - \left[8\Delta H_f(C(gas)) + 18\Delta H_f(H(gas))\right]\right\} \\ &= -\left\{-2.1609\ eV - \left[(8)7.42774\ eV + (18)2.259353\ eV\right]\right\} \\ &= 102.25\ eV \end{aligned} \tag{14.657}$$

The charge-density of the C_8H_{18} MO comprising a linear combination of two methyl and six methylene groups is shown in Figure 55.

NONANE (C_9H_{20})

Using Eq. (14.642) with $n = 9$, the total bond dissociation energy of C_9H_{20} is

$$E_D(C_9H_{20}) = E_D(C-C)_8 + 2E_{D_{alkane}}(^{12}CH_3) + 7E_{D_{alkane}}(^{12}CH_2)$$
$$= (8)(4.32754\ eV) + (2)(12.49186\ eV) + (7)(7.83016\ eV) \quad (14.658)$$
$$= 114.41516\ eV$$

Using Eq. (14.643), the experimental total bond dissociation energy of C_9H_{20}, $E_{D_{exp}}(C_9H_{20})$, given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_9H_{20}(gas) = -2.3651\ eV)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms is

$$E_{D_{exp}}(C_9H_{20}) = -\left\{\Delta H_f(C_9H_{20}(gas)) - \left[9\Delta H_f(C(gas)) + 20\Delta H_f(H(gas))\right]\right\}$$
$$= -\left\{-2.3651\ eV - \left[(9)7.42774\ eV + (20)2.259353\ eV\right]\right\}$$
$$= 114.40\ eV$$

(14.659)

The charge-density of the C_9H_{20} MO comprising a linear combination of two methyl and seven methylene groups is shown in Figure 56.

DECANE ($C_{10}H_{22}$)

Using Eq. (14.642) with $n = 10$, the total bond dissociation energy of $C_{10}H_{22}$ is

$$E_D(C_{10}H_{22}) = E_D(C-C)_9 + 2E_{D_{alkane}}(^{12}CH_3) + 8E_{D_{alkane}}(^{12}CH_2)$$
$$= (9)(4.32754\ eV) + (2)(12.49186\ eV) + (8)(7.83016\ eV) \quad (14.660)$$
$$= 126.57286\ eV$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_{10}H_{22}$, $E_{D_{exp}}(C_{10}H_{22})$, given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_{10}H_{22}(gas) = -2.5858\ eV)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms is

$$E_{D_{exp}}(C_{10}H_{22}) = -\left\{\Delta H_f(C_{10}H_{22}(gas)) - \left[10\Delta H_f(C(gas)) + 22\Delta H_f(H(gas))\right]\right\}$$
$$= -\left\{-2.5858\ eV - \left[(10)7.42774\ eV + (22)2.259353\ eV\right]\right\}$$
$$= 126.57\ eV$$

(14.661)

The charge-density of the $C_{10}H_{22}$ molecular orbital (MO) comprising a linear combination of two methyl and eight methylene groups is shown in Figure 57.

UNDECANE ($C_{11}H_{24}$)

Using Eq. (14.642) with $n=11$, the total bond dissociation energy of $C_{11}H_{24}$ is

$$\begin{aligned} E_D(C_{11}H_{24}) &= E_D(C-C)_{10} + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 9E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (10)(4.32754\ eV) + (2)(12.49186\ eV) + (9)(7.83016\ eV) \\ &= 138.73056\ eV \end{aligned} \tag{14.662}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_{11}H_{24}$, $E_{D_{exp}}(C_{11}H_{24})$, given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_{11}H_{24}(gas) = -2.8066\ eV)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms is

$$\begin{aligned} E_{D_{exp}}(C_{11}H_{24}) &= -\left\{\Delta H_f(C_{11}H_{24}(gas)) - \left[11\Delta H_f(C(gas)) + 24\Delta H_f(H(gas))\right]\right\} \\ &= -\left\{-2.8066\ eV - \left[(11)7.42774\ eV + (24)2.259353\ eV\right]\right\} \\ &= 138.736\ eV \end{aligned} \tag{14.663}$$

The charge-density of the $C_{11}H_{24}$ MO comprising a linear combination of two methyl and nine methylene groups is shown in Figure 58.

DODECANE ($C_{12}H_{26}$)

Using Eq. (14.642) with $n=12$, the total bond dissociation energy of $C_{12}H_{26}$ is

$$\begin{aligned} E_D(C_{12}H_{26}) &= E_D(C-C)_{11} + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + 10E_{D_{alkane}}\left({}^{12}CH_2\right) \\ &= (11)(4.32754\ eV) + (2)(12.49186\ eV) + (10)(7.83016\ eV) \\ &= 150.88826\ eV \end{aligned} \tag{14.664}$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_{12}H_{26}$, $E_{D_{exp}}(C_{12}H_{26})$, given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_{12}H_{26}(gas) = -2.9994\ eV)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms is

$$E_{D_{exp}}(C_{12}H_{26}) = -\left\{\Delta H_f(C_{12}H_{26}(gas)) - \left[12\Delta H_f(C(gas)) + 26\Delta H_f(H(gas))\right]\right\}$$
$$= -\left\{-2.9994\ eV - \left[(12)7.42774\ eV + (26)2.259353\ eV\right]\right\} \quad (14.665)$$
$$= 150.88\ eV$$

The charge-density of the $C_{12}H_{26}$ MO comprising a linear combination of two methyl and ten methylene groups is shown in Figure 59.

OCTADECANE ($C_{18}H_{38}$)

Using Eq. (14.642) with $n = 18$, the total bond dissociation energy of $C_{18}H_{38}$ is

$$E_D(C_{18}H_{38}) = E_D(C-C)_{17} + 2E_{D_{alkane}}(^{12}CH_3) + 16E_{D_{alkane}}(^{12}CH_2)$$
$$= (17)(4.32754\ eV) + (2)(12.49186\ eV) + (16)(7.83016\ eV) \quad (14.666)$$
$$= 223.83446\ eV$$

Using Eq. (14.643), the experimental total bond dissociation energy of $C_{18}H_{38}$, $E_{D_{exp}}(C_{18}H_{38})$, given by the negative difference between the enthalpy of its formation ($\Delta H_f(C_{18}H_{38}(gas) = -4.2970\ eV)$) [18] and the sum of the enthalpy of the formation of the gaseous carbons ($\Delta H_f(C(gas))$) and hydrogen ($\Delta H_f(H(gas))$) atoms is

$$E_{D_{exp}}(C_{18}H_{38}) = -\left\{\Delta H_f(C_{18}H_{38}(gas)) - \left[18\Delta H_f(C(gas)) + 38\Delta H_f(H(gas))\right]\right\}$$
$$= -\left\{-4.2970\ eV - \left[(18)7.42774\ eV + (38)2.259353\ eV\right]\right\}$$
$$= 223.85\ eV$$

(14.667)

The charge-density of the $C_{18}H_{38}$ molecular orbital (MO) comprising a linear combination of two methyl and sixteen methylene groups is shown in Figure 60.

Table 14.1. The calculated and experimental bond parameters of CO_2, NO_2, CH_3CH_3, CH_2CH_2, $CHCH$, benzene, propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and octadecane.

Parameter	Calculated	Experimental	Ref. for Exp.
CO_2 Bond Energy	5.49553 eV	5.51577 eV	7
CO_2 Bond Length	1.1616 Å	1.1600 Å	3

Parameter	Calculated	Experimental	Ref. for Exp.
NO_2 Bond Energy	3.1532 eV	3.161 eV	7
NO_2 Bond Length	1.1872 Å	1.193 Å	3
NO_2 Bond Angle	131.012°	134.1°	3
H_3C-CH_3 Bond Energy	3.90245 eV	3.8969 eV	7
H_3C-CH_3 Bond Length	1.53635 Å	1.5351 Å	3
$H-CH_2CH_3$ Bond Length	1.10822 Å	1.0940 Å	3
Ethane $H-C-H$ Bond Angle	107.44°	107.4°	8
Ethane $C-C-H$ Bond Angle	111.44°	111.17°	3
$H_2C=CH_2$ Bond Energy	7.55681 eV	7.597 eV	7
$H_2C=CH_2$ Bond Length	1.3405 Å	1.339 Å	3
$H-CHCH_2$ Bond Length	1.0826 Å	1.087 Å	3
Ethylene $H-C-H$ Bond Angle	116.31°	116.6°	11
Ethylene $C=C-H$ Bond Angle	121.85°	121.7°	11
$HC\equiv CH$ Bond Energy	10.07212 eV	10.0014 eV	7
$HC\equiv CH$ Bond Length	1.2007 Å	1.203 Å	3
$H-CCH$ Bond Length	1.0538 Å	1.060 Å	3
Acetylene $C\equiv C-H$ Bond Angle	180°	180°	6
C_6H_6 Total Bond Energy	57.2601 eV	57.26 eV	17-18
Benzene $C=C$ Bond Length	1.3914 Å	1.399 Å	3
$H-C_6H_5$ Bond Length	1.0933 Å	1.101 Å	3
C_6H_6 $C=C=C$ Bond Angle	120°	120°	13-15
C_6H_6 $C=C-H$ Bond Angle	120°	120°	13-15
C_3H_8 Total Bond Energy	41.46896 eV	41.434 eV	17-18
Propane $C-C$ Bond Length	1.5428 Å	1.532 Å	3
Propane $C-H$ Bond Length	1.1097 Å	1.107 Å	3
Alkane $H-C-H$ Bond Angle	109.50°	109.3°	19
Alkane $C-C-H$ Bond Angle	109.44°	109.3°	19
C_4H_{10} Total Bond Energy	53.62666 eV	53.61 eV	17-18
Butane $C-C$ Bond Length	1.5428 Å	1.531 Å	3
Butane $C-H$ Bond Length	1.11713 Å	1.117 Å	3

Parameter	Calculated	Experimental	Ref. for Exp.
C_5H_{12} Total Bond Energy	65.78436 eV	65.77 eV	17-18
C_6H_{14} Total Bond Energy	77.94206 eV	77.93 eV	17-18
C_7H_{16} Total Bond Energy	90.09976 eV	90.09 eV	17-18
C_8H_{18} Total Bond Energy	102.25746 eV	102.25 eV	17-18
C_9H_{20} Total Bond Energy	114.41516 eV	114.40 eV	17-18
$C_{10}H_{22}$ Total Bond Energy	126.57286 eV	126.57 eV	17-18
$C_{11}H_{24}$ Total Bond Energy	138.73056 eV	138.736 eV	17-18
$C_{12}H_{26}$ Total Bond Energy	150.88826 eV	150.88 eV	17-18
$C_{18}H_{38}$ Total Bond Energy	223.83446 eV	223.85 eV	17-18

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Section IV

ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

Organic molecules comprising an arbitrary number of atoms can be solved using the similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of CH_3, CH_2, and $C-C$. These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkynes, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides, urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfones, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by using generalized forms of the geometrical and energy equations. The equations and sections that are referenced by not contained in this text refer to those sections and equations of the book by R. L. Mills entitled, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at **http://www.blacklightpower.com/bookdownload.shtml** which is incorporated in its entirety by reference.

Consider the case wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force generalized constant k' of a

H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.1}$$

where C_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of H bonding to a central atom and 0.5 (Eq. (14.152)) otherwise, and C_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}} \tag{15.2}$$

The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1 C_2}} \tag{15.3}$$

The length of the semiminor axis of the prolate spheroidal MO $b = c$ is given by

$$b = \sqrt{a^2 - c'^2} \tag{15.4}$$

And, the eccentricity, e, is

$$e = \frac{c'}{a} \tag{15.5}$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2 - b^2}} \ln\frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \tag{15.6}$$

The potential energy of the two nuclei is

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2 - b^2}} \tag{15.7}$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln\frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \tag{15.8}$$

And, the energy, V_m, of the magnetic force between the electrons is

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4 m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \tag{15.9}$$

The total energy of the H_2-type prolate spheroidal MO, $E_T(H_2MO)$, is given by the sum of the energy terms:

$$E_T(H_2MO) = V_e + T + V_m + V_p \tag{15.10}$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \left[c_1 c_2 \left(2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] \\ &= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'} \left[c_1 c_2 \left(2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \end{aligned} \tag{15.11}$$

where n_1 is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by c_{BO}, the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules, and 9 for an independent triplet bond. Then, the kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. c_1 is the fraction of the H_2-type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of H bonding to an unhybridized central atom and 1 otherwise, and c_2 is the factor that results in an equipotential energy match of the participating the MO and the at least two atomic orbitals of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the H_2-type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor c_2 of a H_2-type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of H, (iii) the ratio of the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two c_2 factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different c_2 factors corresponding to any of the cases (i)-(v). Specific examples of the factor c_2 of a H_2-type ellipsoidal MO given in previous sections are

0.936127, the ratio of the ionization energy of N 14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.91771, the ratio of 14.82575 eV, $-E_{Coulomb}\left(C,2sp^3\right)$, and 13.605804 eV;

0.87495, the ratio of 15.55033 eV, $-E_{Coulomb}\left(C_{ethane},2sp^3\right)$, and 13.605804 eV;

0.85252, the ratio of 15.95955 eV, $-E_{Coulomb}\left(C_{ethylene},2sp^3\right)$, and 13.605804 eV;

0.85252, the ratio of 15.95955 eV, $-E_{Coulomb}\left(C_{benzene},2sp^3\right)$, and 13.605804 eV, and

0.86359, the ratio of 15.55033 eV, $-E_{Coulomb}\left(C_{alkane},2sp^3\right)$, and 13.605804 eV.

In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy $E_T\left(atom,msp^3\right)$ (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one AO shell.

$$E_T\left(atom,msp^3\right)=-\sum_{m=1}^{n}IP_m \tag{15.12}$$

where IP_m is the mth ionization energy (positive) of the atom. The radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3}=\sum_{q=Z-n}^{Z-1}\frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T\left(atom,msp^3\right)} \tag{15.13}$$

Then, the Coulombic energy $E_{Coulomb}\left(atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by

$$E_{Coulomb}\left(atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} \tag{15.14}$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r of the AO electron:

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3}=\frac{8\pi\mu_o\mu_B^2}{r^3} \tag{15.15}$$

Then, the energy $E\left(atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(atom,msp^3\right)$ and $E(magnetic)$:

$$E\left(atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} \tag{15.16}$$

Consider next that the at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the hybridized orbitals is given by the sum of $E\left(atom,msp^3\right)$ and the next energies of successive ions of the atom over the n electrons comprising the total electrons of the at least two initial AO shells. Here, $E\left(atom,msp^3\right)$ is the sum of the first ionization energy of the atom and the hybridization energy. An example of $E\left(atom,msp^3\right)$ for $E\left(C,2sp^3\right)$ is given in Eq. (14.503) where the sum of the negative of the first ionization energy of C, $-11.27671\ eV$, plus the hybridization energy to form the $C2sp^3$ shell given by Eq. (14.146) is $E\left(C,2sp^3\right)=-14.63489\ eV$.

Thus, the sharing of electrons between two *atom* msp^3 HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each *atom* msp^3 HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy $E_T\left(mol.atom,msp^3\right)$ (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$E_T\left(mol.atom,msp^3\right)=E\left(atom,msp^3\right)-\sum_{m=2}^{n}IP_m \tag{15.17}$$

where IP_m is the mth ionization energy (positive) of the atom and the sum of $-IP_1$ plus the hybridization energy is $E\left(atom,msp^3\right)$. Thus, the radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3}=\left(\sum_{q=Z-n}^{Z-1}(Z-q)-s(0.25)\right)\frac{-e^2}{8\pi\varepsilon_0 E_T\left(mol.atom,msp^3\right)} \tag{15.18}$$

where $s=1,2,3$ for a single, double, and triple bond, respectively. The Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by

$$E_{Coulomb}\left(mol.atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} \tag{15.19}$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r of the AO electron given by Eq. (15.15). Then, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$:

$$E\left(mol.atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} \tag{15.20}$$

$E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between $E\left(mol.atom,msp^3\right)$ and $E\left(atom,msp^3\right)$:

$$E_T\left(atom-atom,msp^3\right)=E\left(mol.atom,msp^3\right)-E\left(atom,msp^3\right) \tag{15.21}$$

As examples from prior sections, $E_{Coulomb}\left(mol.atom,msp^3\right)$ is one of:

$E_{Coulomb}\left(C_{ethylene},2sp^3\right)$, $E_{Coulomb}\left(C_{ethane},2sp^3\right)$, $E_{Coulomb}\left(C_{acetylene},2sp^3\right)$, and $E_{Coulomb}\left(C_{alkane},2sp^3\right)$;

$E_{Coulomb}\left(atom,msp^3\right)$ is one of $E_{Coulomb}\left(C,2sp^3\right)$ and $E_{Coulomb}\left(Cl,3sp^3\right)$;

$E\left(mol.atom,msp^3\right)$ is one of $E\left(C_{ethylene},2sp^3\right)$, $E\left(C_{ethane},2sp^3\right)$, $E\left(C_{acetylene},2sp^3\right)E\left(C_{alkane},2sp^3\right)$;

$E\left(atom,msp^3\right)$ is one of and $E\left(C,2sp^3\right)$ and $E\left(Cl,3sp^3\right)$;

$E_T\left(atom-atom,msp^3\right)$ is one of $E\left(C-C,2sp^3\right)$, $E\left(C=C,2sp^3\right)$, and. $E\left(C\equiv C,2sp^3\right)$;

$atom\ msp^3$ is one of $C2sp^3$, $Cl3sp^3$

$E_T\left(atom-atom(s_1),msp^3\right)$ is $E_T\left(C-C,2sp^3\right)$ and $E_T\left(atom-atom(s_2),msp^3\right)$ is $E_T\left(C=C,2sp^3\right)$, and

r_{msp^3} is one of r_{C2sp^3}, $r_{ethane2sp^3}$, $r_{ethylene2sp^3}$, $r_{acetylene2sp^3}$, $r_{alkane2sp^3}$, and r_{Cl3sp^3}.

In the case of the $C2sp^3$ HO, the initial parameters (Eqs. (14.142-14.146)) are

$$r_{2sp^3}=\sum_{n=2}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)}=\frac{10e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)}=0.91771a_0 \tag{15.22}$$

$$E_{Coulomb}\left(C,2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.91771a_0}=-14.82575\ eV \tag{15.23}$$

$$E(magnetic)=\frac{2\pi\mu_0 e^2\mathrm{h}^2}{m_e^2\left(r_3\right)^3}=\frac{8\pi\mu_o\mu_B^2}{\left(0.84317a_0\right)^3}=0.19086\ eV \tag{15.24}$$

$$\begin{aligned}E\left(C,2sp^3\right)&=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}+\frac{2\pi\mu_0 e^2\mathrm{h}^2}{m_e^2\left(r_3\right)^3}\\&=-14.82575\ eV+0.19086\ eV\\&=-14.63489\ eV\end{aligned} \tag{15.25}$$

In Eq. (15.18),

$$\sum_{q=Z-n}^{Z-1}(Z-q)=10 \tag{15.26}$$

Eqs. (14.147) and (15.17) give

$$E_T\left(mol.atom,msp^3\right)=E_T\left(C_{ethane},2sp^3\right)=-151.61569\ eV \tag{15.27}$$

Using Eqs. (15.18-15.28), the final values of r_{C2sp^3}, $E_{Coulomb}\left(C2sp^3\right)$, and $E\left(C2sp^3\right)$, and the resulting $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ of the MO due to charge donation from the HO to the MO where

$\overset{BO}{C-C}$ refers to the bond order of the carbon-carbon bond for different values of the parameter s are given in Table 15.1.

Table 15.1. The final values of r_{C2sp^3}, $E_{Coulomb}\left(C2sp^3\right)$, and $E\left(C2sp^3\right)$ and the resulting $E_T\left(\overset{BO}{C-C},C2sp^3\right)$ of the MO due to charge donation from the HO to the MO where $\overset{BO}{C-C}$ refers to the bond order of the carbon-carbon bond.

MO Bond Order (BO)	s 1	s 2	$r_{C2sp^3}\left(a_0\right)$ Final	$E_{Coulomb}\left(C2sp^3\right)$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	$E_T\left(\overset{BO}{C-C},C2sp^3\right)$ (eV)
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
II	2	0	0.85252	-15.95955	-15.76868	-1.13379
III	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell of each bonding atom must be the average of $E\left(mol.atom,msp^3\right)$ for two different values of s:

$$E\left(mol.atom,msp^3\right)=\frac{E\left(mol.atom\left(s_1\right),msp^3\right)+E\left(mol.atom\left(s_2\right),msp^3\right)}{2} \tag{15.28}$$

In this case, $E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO, is average for two different values of s:

$$E_T\left(atom-atom,msp^3\right)=\frac{E_T\left(atom-atom\left(s_1\right),msp^3\right)+E_T\left(atom-atom\left(s_2\right),msp^3\right)}{2} \tag{15.29}$$

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each $C=C$ double bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ bond of CH having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the

linear combination of 75% H_2-type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.439). However, $E_T\left(atom-atom,msp^3\right)$ of the $C-H$-bond MO is given by $0.5E_T\left(C=C,2sp^3\right)$ (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for $C-H$ that is lowered in energy due to the aromatic character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of H_2-type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75, 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general, $E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO, is a weighted linear sum for different values of s that matches the energy of the bonded MOs, HOs, and AOs:

$$E_T\left(atom-atom,msp^3\right)=\sum_{n=1}^{N}c_{s_n}E_T\left(atom-atom\left(s_n\right),msp^3\right) \tag{15.30}$$

where c_{s_n} is the multiple of the BO of s_n. The radius r_{msp^3} of the *atom* msp^3 shell of each bonding atom is given by the Coulombic energy using the initial energy $E_{Coulomb}\left(atom,msp^3\right)$ and $E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO:

$$r_{msp^3}=\frac{-e^2}{8\pi\varepsilon_0 a_0\left(E_{Coulonb}\left(atom,msp^3\right)+E_T\left(atom-atom,msp^3\right)\right)} \tag{15.31}$$

where $E_{Coulomb}\left(C2sp^3\right)=-14.825751\ eV$. The Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)). $E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between $E\left(mol.atom,msp^3\right)$ and $E\left(atom,msp^3\right)$ given by Eq. (15.21). Using Eq. (15.23) for $E_{Coulomb}\left(C,2sp^3\right)$ in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

Table 15.2. The final values of r_{C2sp^3}, $E_{Coulomb}\left(C2sp^3\right)$, and $E\left(C2sp^3\right)$ and the resulting $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ of the MO comprising a linear combination of H_2-type ellipsoidal MOs and corresponding HOs of single or mixed bond order where c_{s_n} is the multiple of the bond order parameter $E_T\left(atom-atom\left(s_n\right),msp^3\right)$ given in Table 15.1.

Table 15.1

MO Bond Order (BO)	s 1	c_{s_1}	s 2	c_{s_2}	s 3	c_{s_3}	$r_{C2sp^3}(a_0)$ Final	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	$E_T\left(C-C,C2sp^3\right)$ (eV)
1/2I	1	0.5	0	0	0	0	0.89582	-15.18804	-14.99717	-0.36228
1/2II	2	0.5	0	0	0	0	0.88392	-15.39265	-15.20178	-0.56689
I + 1/2II	1	0.5	2	0.25	0	0	0.87941	-15.47149	-15.28062	-0.64573
1/2II + (I + II)	2	0.25	1	0.25	2	0.25	0.87363	-15.57379	-15.38293	-0.74804
3/4II	2	0.75	0	0	0	0	0.86793	-15.67610	-15.48523	-0.85034
I + II	1	0.5	2	0.5	0	0	0.86359	-15.75493	-15.56407	-0.92918
I + III	1	0.5	3	0.5	0	0	0.85193	-15.97060	-15.77974	-1.14485
I + IV	1	0.5	4	0.5	0	0	0.83995	-16.19826	-16.00739	-1.37250
II + III	2	0.5	3	0.5	0	0	0.84115	-16.17521	-15.98435	-1.34946
II + IV	2	0.5	4	0.5	0	0	0.82948	-16.40286	-16.21200	-1.57711
III + IV	3	0.5	4	0.5	0	0	0.81871	-16.61853	-16.42767	-1.79278
IV + IV	4	0.5	4	0.5	0	0	0.80765	-16.84619	-16.65532	-2.02043

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as carbon superimposes linearly. In general, the radius r_{mol2sp^3} of the $C2sp^3$ HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$r_{mol2sp^3} = \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{mol}}\left(MO,2sp^3\right)\right)} = \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+\sum\left|E_{T_{mol}}\left(MO,2sp^3\right)\right|\right)} \tag{15.32}$$

The Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

For example, the $C2sp^3$ HO of each methyl group of an alkane contributes $-0.92918\ eV$ (Eq. (14.513)) to the corresponding single $C-C$ bond; thus, the corresponding $C2sp^3$ HO radius is given by Eq. (14.514). The $C2sp^3$ HO of each methylene group of C_nH_{2n+2} contributes $-0.92918\ eV$ to each of the two corresponding $C-C$ bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

$$r_{alkaneC_{methylene}2sp^3} = \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{alkane}}\left(methylene\ C-C,2sp^3\right)\right)} = \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+e0.92918\ eV+e0.92918\ eV\right)} = 0.81549a_0 \tag{15.33}$$

$$E_{Coulomb}\left(C_{methylene}2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0\left(0.81549a_0\right)} = -16.68412\ eV \tag{15.34}$$

$$E\left(C_{methylene}2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0\left(0.81549a_0\right)} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(0.84317a_0\right)^3} = -16.49325\ eV \tag{15.35}$$

In the determination of the parameters of functional groups, heteroatoms bonding to $C2sp^3$ HOs to form MOs are energy matched to the $C2sp^3$ HOs. Thus, the radius and the energy parameters of a bonding heteroatom are given by the same equations as those for

$C2sp^3$ HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO, $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom, msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ are calculated using $\sum E_{T_{group}}\left(MO, 2sp^3\right)$, the total energy donation to each bond with which an atom participates in bonding corresponding to the values of $E_T\left(C\overset{BO}{-}C, C2sp^3\right)$ of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom, msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ calculated using the values of $E_T\left(C\overset{BO}{-}C, C2sp^3\right)$ given in Tables 15.1 and 15.2.

Atom Hybridization Designation	$E_T\left(C-C,C2sp^3\right)^{BO}$	$E_T\left(C-C,C2sp^3\right)^{BO}$	$E_T\left(C-C,C2sp^3\right)^{BO}$	$E_T\left(C-C,C2sp^3\right)^{BO}$	$E_T\left(C-C,C2sp^3\right)^{BO}$	$r_{Atom.HO.AO}$ Final	$E_{Coulomb}\left(mol.atom,msp^3\right)$ (eV) Final	$E\left(C_{mol}2sp^3\right)$ (eV) Final
1	0	0	0	0	0	0.91771	-14.82575	-14.63489
2	-0.36229	0	0	0	0	0.89582	-15.18804	-14.99717
3	-0.46459	0	0	0	0	0.88983	-15.29034	-15.09948
4	-0.56689	0	0	0	0	0.88392	-15.39265	-15.20178
5	-0.72457	0	0	0	0	0.87495	-15.55033	-15.35946
6	-0.85034	0	0	0	0	0.86793	-15.6761	-15.48523
7	-0.92918	0	0	0	0	0.86359	-15.75493	-15.56407
8	-0.54343	-0.54343	0	0	0	0.85503	-15.91261	-15.72175
9	-1.13379	0	0	0	0	0.85252	-15.95955	-15.76868
10	-1.14485	0	0	0	0	0.85193	-15.9706	-15.77974
11	-0.46459	-0.82688	0	0	0	0.84418	-16.11722	-15.92636
12	-1.34946	0	0	0	0	0.84115	-16.17521	-15.98435
13	-1.3725	0	0	0	0	0.83995	-16.19826	-16.00739
14	-0.46459	-0.92918	0	0	0	0.83885	-16.21952	-16.02866
15	-0.72457	-0.72457	0	0	0	0.836	-16.2749	-16.08404
16	-0.5669	-0.92918	0	0	0	0.8336	-16.32183	-16.13097
17	-0.82688	-0.72457	0	0	0	0.83078	-16.37721	-16.18634
18	-1.56513	0	0	0	0	0.83008	-16.39089	-16.20002
19	-0.64574	-0.92918	0	0	0	0.82959	-16.40067	-16.20981
20	-1.57711	0	0	0	0	0.82948	-16.40286	-16.212
21	-0.72457	-0.92918	0	0	0	0.82562	-16.47951	-16.28865
22	-0.85035	-0.85035	0	0	0	0.82327	-16.52645	-16.33559
23	-1.79278	0	0	0	0	0.81871	-16.61853	-16.42767
24	-1.13379	-0.72457	0	0	0	0.81549	-16.68411	-16.49325
25	-0.92918	-0.92918	0	0	0	0.81549	-16.68412	-16.49325
26	-2.02043	0	0	0	0	0.80765	-16.84619	-16.65532

27	-1.13379	-0.92918	0	0	0	0.80561	-16.88872	-16.69786	
28	-0.85035	-0.85035	-0.46459	0	0	0.80076	-16.99104	-16.80018	
29	-0.5669	-0.72457	-0.92918	0	0	0.78916	-17.04641	-16.85554	
30	-1.13379	-1.13379	0	0	0	0.79597	-17.09334	-16.90248	
31	-1.34946	-0.92918	0	0	0	0.79546	-17.1044	-16.91353	
32	-0.46459	-0.92918	-0.92918	0	0	0.79340	-17.14871	-16.95784	
33	-0.64574	-0.85034	-0.85034	0	0	0.79232	-17.17217	-16.98131	
34	-0.85035	-0.5669	-0.92918	0	0	0.79232	-17.17218	-16.98132	
35	-0.72457	-0.72457	-0.92918	0	0	0.79085	-17.20408	-17.01322	
36	-0.82688	-0.72457	-0.92918	0	0	0.78617	-17.30638	-17.11552	
37	-0.72457	-0.92918	-0.92918	0	0	0.78155	-17.40868	-17.21782	
38	-0.92918	-0.72457	-0.92918	0	0	0.78155	-17.40869	-17.21783	
39	-0.54343	-0.54343	-0.5669	-0.92918	0	0.78155	-17.40869	-17.21783	
40	-0.92918	-0.85034	-0.85034	0	0	0.77945	-17.45561	-17.26475	
41	-0.82688	-0.92918	-0.92918	0	0	0.77699	-17.51099	-17.32013	
42	-0.92918	-0.92918	-0.92918	0	0	0.77247	-17.6133	-17.42244	
43	-0.85035	-0.54343	-0.5669	-0.92918	0	0.76801	-17.71561	-17.52475	
44	-1.34946	-0.64574	-0.92918	0	0	0.76652	-17.75013	-17.55927	
45	-0.85034	-0.54343	-0.60631	-0.92918	0	0.76631	-17.75502	-17.56415	
46	-1.1338	-0.92918	-0.92918	0	0	0.7636	-17.81791	-17.62705	
47	-0.46459	-0.85035	-0.85035	-0.92918	0	0.75924	-17.92022	-17.72936	
48	-0.82688	-1.34946	-0.92918	0	0	0.75877	-17.93128	-17.74041	
49	-1.13379	-1.13379	-1.13379	0	0	0.74646	-18.22712	-18.03626	
50	-1.79278	-0.92918	-0.92918	0	0	0.73637	-18.47690	-18.28604	

Table 15.3.B. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom, msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ calculated for heterocyclic groups using the values of $E_T\left(C\overset{BO}{-}C, C2sp^3\right)$ given in Tables 15.1 and 15.2.

Atom Hybridization Designation	$E_T\left(C-C,C2sp^3\right)^{BO}$	$E_r\left(C-C,C2sp^3\right)^{BO}$	$E_r\left(C-C,C2sp\right)^{BO}$	$E_T\left(C-C,C2sp^3\right)^{BO}$	$E_r\left(C-C,C2sp^3\right)^{BO}$	$r'_{Atom.HO.AO}$ Final	$E_{Coulomb}\left(mol.atom,msp^3\right)$ (eV) Final	$E\left(C_{mol}2sp^3\right)$ (eV) Final
1	0	0	0	0	0	0.91771	-14.82575	-14.63489
2	-0.56690	0	0	0	0	0.88392	-15.39265	-15.20178
3	-0.72457	0	0	0	0	0.87495	-15.55033	-15.35946
4	-0.92918	0	0	0	0	0.86359	-15.75493	-15.56407
5	-0.54343	-0.54343	0	0	0	0.85503	-15.91261	-15.72175
6	-1.13379	0	0	0	0	0.85252	-15.95954	-15.76868
7	-0.60631	-0.60631	0	0	0	0.84833	-16.03838	-15.84752
8	-0.46459	-0.92918	0	0	0	0.83885	-16.21953	-16.02866
9	-0.72457	-0.72457	0	0	0	0.83600	-16.27490	-16.08404
10	-0.92918	-0.60631	0	0	0	0.83159	-16.36125	-16.17038
11	-0.92918	-0.72457	0	0	0	0.82562	-16.47951	-16.28864
12	-0.85035	-0.85035	0	0	0	0.82327	-16.52644	-16.33558
13	-0.92918	-0.92918	0	0	0	0.81549	-16.68411	-16.49325
14	-1.13379	-0.72457	0	0	0	0.81549	-16.68412	-16.49325
15	-1.13379	-0.92918	0	0	0	0.80561	-16.88873	-16.69786
16	-0.85035	-0.85035	-0.46459	0	0	0.80076	-16.99103	-16.80017
17	-0.85034	-0.85034	-0.56690	0	0	0.79597	-17.09334	-16.90247
18	-1.13379	-1.13380	0	0	0	0.79597	-17.09334	-16.90248
19	-0.85035	-0.54343	0.00000	-0.92918	0	0.79340	-17.14871	-16.95785
20	-0.85035	-0.56690	-0.92918	0	0	0.79232	-17.17218	-16.98132
21	-0.54343	-0.54343	-0.56690	-0.92918	0	0.78155	-17.40869	-17.21783
22	-0.85034	-0.28345	-0.54343	-0.92918	0	0.78050	-17.43216	-17.24130
23	-0.92918	-0.92918	-0.92918	0	0	0.77247	-17.61330	-17.42243
24	-0.85034	-0.54343	-0.56690	-0.92918	0	0.76801	-17.71560	-17.52474
25	-0.85034	-0.54343	-0.60631	-0.92918	0	0.76631	-17.75502	-17.56416
26	-1.13379	-0.92918	-0.92918	0	0	0.76360	-17.81791	-17.62704

27	-1.13379	-1.13380	-0.72457	0	0	0.76360	-17.81791	-17.62705
28	-0.46459	-0.85035	-0.85035	-0.92918	0	0.75924	-17.92022	-17.72935
29	-1.13380	-1.13379	-0.92918	0	0	0.75493	-18.02252	-17.83166
30	-1.13379	-1.13379	-1.13379	0	0	0.74646	-18.22713	-18.03627

The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant k' (Eq. (15.1)) is used to determine the ellipsoidal parameter c' (Eq. (15.2)) of the each H_2-type-ellipsoidal-MO in terms of the central force of the foci. Then, c' is substituted into the energy equation (from Eq. (15.11))) which is set equal to n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2, $-31.63536831\,eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis a as it only parameter. The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy, $E_T(H_2MO)$, is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus $E_T(AO/HO)$:

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO) \tag{15.36}$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E_T(AO/HO) \\ &= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T(AO/HO) \end{aligned} \tag{15.37}$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the group, c_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and $E_T(AO/HO)$ is the total energy comprising the difference of the energy $E(AO/HO)$ of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component $\Delta E_{H_2MO}(AO/HO)$ due to the AO or HO's charge donation to the MO.

$$E_T(AO/HO) = E(AO/HO) - \Delta E_{H_2MO}(AO/HO) \tag{15.38}$$

As specific examples given in previous sections, $E_T(AO/HO)$ is one from the group of

$$E_T(AO/HO)=E(O2p\ shell)=-E(ionization;\ O)=-13.6181\ eV;$$

$$E_T(AO/HO)=E(N2p\ shell)=-E(ionization;\ N)=-14.53414\ eV;$$

$$E_T(AO/HO)=E(C,2sp^3)=-14.63489\ eV;$$

$$E_T(AO/HO)=E_{Coulomb}(Cl,3sp^3)=-14.60295\ eV;$$

$$E_T(AO/HO)=E(ionization;\ C)+E(ionization;\ C^+);$$

$$E_T(AO/HO)=E(C_{ethane},2sp^3)=-15.35946\ eV;$$

$$E_T(AO/HO)=+E(C_{ethylene},2sp^3)-E(C_{ethylene},2sp^3);$$

$$E_T(AO/HO)=E(C,2sp^3)-2E_T(C=C,2sp^3)=-14.63489\ eV-(-2.26758\ eV);$$

$$E_T(AO/HO)=E(C_{acetylene},2sp^3)-E(C_{acetylene},2sp^3)-E(C_{acetylene},2sp^3)=16.20002\ eV;$$

$$E_T(AO/HO)=E(C,2sp^3)-2E_T(C\equiv C,2sp^3)=-14.63489\ eV-(-3.13026\ eV);$$

$$E_T(AO/HO)=E(C_{benzene},2sp^3)-E(C_{benzene},2sp^3);$$

$$E_T(AO/HO)=E(C,2sp^3)-E_T(C=C,2sp^3)=-14.63489\ eV-(-1.13379\ eV),\ \text{and}$$

$$E_T(AO/HO)=E(C_{alkane},2sp^3)=-15.56407\ eV.$$

To solve the bond parameters and energies, $c'=a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}}=\sqrt{\frac{aa_0}{2C_1C_2}}$ (Eq. (15.2)) is substituted into $E_T(H_2MO)$ to give

$$\begin{aligned}E_T(H_2MO)&=-\frac{n_1e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E_T(AO/HO)\\&=-\frac{n_1e^2}{8\pi\varepsilon_0c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T(AO/HO)\\&=-\frac{n_1e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T(AO/HO)\end{aligned}\qquad(15.39)$$

The total energy is set equal to $E(basis\ energies)$ which in the most general case is given by

the sum of a first integer n_1 times the total energy of H_2 minus a second integer n_2 times the total energy of H, minus a third integer n_3 times the valence energy of $E(AO)$ (e.g. $E(N)=-14.53414\ eV$) where the first integer can be $1,2,3...$, and each of the second and third integers can be $0,1,2,3....$

$$E(basis\ energies)=n_1(-31.63536831\ eV)-n_2(-13.605804\ eV)-n_3E(AO) \quad (15.40)$$

In the case that the MO bonds two atoms other than hydrogen, $E(basis\ energies)$ is n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2, $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

$$E(basis\ energies)=n_1(-31.63536831\ eV) \quad (15.41)$$

$E_T(H_2MO)$, is set equal to $E(basis\ energies)$, and the semimajor axis a is solved. Thus, the semimajor axis a is solved from the equation of the form:

$$-\frac{n_1e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T(AO/HO)=E(basis\ energies) \quad (15.42)$$

The distance from the origin of the H_2-type-ellipsoidal-MO to each focus c', the internuclear distance $2c'$, and the length of the semiminor axis of the prolate spheroidal H_2-type MO $b=c$ are solved from the semimajor axis a using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.39).

The total energy of the MO of the functional group, $E_T(MO)$, is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and $E_T(atom-atom,msp^3.AO)$, the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.39-15.40), $E_T(MO)$ is

$$E_T(MO)=E(basis\ energies)+E_T(atom-atom,msp^3.AO) \quad (15.43)$$

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the sum of the Doppler, $\overline{E}_D$, and average vibrational kinetic energies, $\overline{E}_{Kvib}$:

$$\bar{E}_{osc} = n_1\left(\bar{E}_D + \bar{E}_{Kvib}\right) = n_1\left(E_{h\nu}\sqrt{\frac{2\bar{E}_K}{m_e c^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.44}$$

where n_1 is the number of equivalent bonds of the MO , k is the spring constant of the equivalent harmonic oscillator, and μ is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to $\bar{E}_D$ is determined by the force between the central field and the electrons in the transition state. The force and its derivative are given by

$$f(R) = -c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.45}$$

and

$$f'(a) = 2c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.46}$$

such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}} \tag{15.47}$$

where R is the semimajor axis a or the semiminor axis b depending on the eccentricity of the bond that is most representative of the oscillation in the transition state, c_{BO} is the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules and 9 for an independent triplet bond. C_{1o} is the fraction of the H_2-type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. Typically, $C_{1o} = C_1$ and $C_{2o} = C_2$. The kinetic energy, E_K, corresponding to $\bar{E}_D$ is given by Planck's equation for functional groups:

$$\bar{E}_K = \hbar\omega = \hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}} \tag{15.48}$$

The Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{m_e c^2}} = E_{hv}\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}}{m_e c^2}} \tag{15.49}$$

$\overline{E}_{osc}$ given by the sum of $\overline{E}_D$ and $\overline{E}_{Kvib}$ is

$$\overline{E}_{osc}(group) = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_{hv}\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}}{m_e c^2}} + E_{vib}\right) \tag{15.50}$$

E_{hv} of a group having n_1 bonds is given by $E_T(MO)/n_1$ such that

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_T(MO)/n_1\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.51}$$

$E_{T+osc}(Group)$ is given by the sum of $E_T(MO)$ (Eq. (15.42)) and $\overline{E}_{osc}$ (Eq. (15.51)):

$$E_{T+osc}(Group) = E_T(MO) + \overline{E}_{osc}$$

$$= \left(\left(\begin{array}{l} -\dfrac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\dfrac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\dfrac{a_0}{a}\right)\ln\dfrac{a+\sqrt{\dfrac{aa_0}{2C_1C_2}}}{a-\sqrt{\dfrac{aa_0}{2C_1C_2}}} - 1\right] \\ +E_T(AO/HO) + E_T(atom-atom, msp^3.AO) \end{array}\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}}\right] + n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$= \left(E(basis\ energies) + E_T(atom-atom, msp^3.AO)\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}}\right] + n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

(15.52)

The total energy of the functional group $E_T(group)$ is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, $E(basis\ energies)$, the change in the energy of the AOs or HOs upon forming the bond ($E_T\left(atom-atom, msp^3.AO\right)$), the energy of oscillation in the transition state, and the change in magnetic energy with bond formation, E_{mag}. From Eq. (15.52), the total energy of the group $E_T(Group)$ is

$$E_T(Group)=\begin{pmatrix}\left(E(basis\ energies)+E_T\left(atom-atom, msp^3.AO\right)\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_e c^2}}\right]\\ +n_1\bar{E}_{Kvib}+E_{mag}\end{pmatrix} \quad (15.53)$$

The change in magnetic energy E_{mag} which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

$$E_{mag}=c_3\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3}=c_3\frac{8\pi\mu_o\mu_B^2}{r^3} \quad (15.54)$$

where r^3 is the radius of the atom that reacts to form the bond and c_3 is the number of electron pairs.

$$E_T(Group)=\begin{pmatrix}\left(E(basis\ energies)+E_T\left(atom-atom, msp^3.AO\right)\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}}{m_e c^2}}\right]\\ +n_1\bar{E}_{Kvib}+c_3\frac{8\pi\mu_o\mu_B^2}{r^3}\end{pmatrix} \quad (15.55)$$

The total bond energy of the group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.55)) and the total energy of the starting species given by the sum of $c_4E_{initial}\left(c_4\ AO/HO\right)$ and $c_5E_{initial}\left(c_5\ AO/HO\right)$:

$$E_D(Group) = -\left(\left(E(basis\ energies) + E_T\left(atom - atom, msp^3.AO\right) \right) \left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}} \right] + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o\mu_B^2}{r_n^3} - \left(c_4 E_{initial}\left(AO/HO\right) + c_5 E_{initial}\left(c_5\ AO/HO\right) \right) \right) \quad (15.56)$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the $C2sp^3$ HO such that

$$E\left(AO/HO\right) = -14.63489\ eV \quad (15.57)$$

For examples of E_{mag} from previous sections:

$$E_{mag}\left(C2sp^3\right) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{\left(0.91771a_0\right)^3} = c_3 0.14803\ eV \quad (15.58)$$

$$E_{mag}\left(O2p\right) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{a_0^3} = c_3 0.11441\ eV \quad (15.59)$$

$$E_{mag}\left(N2p\right) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{\left(0.93084a_0\right)^3} = c_3 0.14185\ eV \quad (15.60)$$

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at a. Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.52-15.59). To meet the equipotential condition for the union of the H_2-type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor c_2 of a H_2-type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

(i) one:

$$c_2 = 1 \quad (15.61)$$

(ii) the ratio that is less than one of $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the

Coulombic energy of the participating AO or HO of the atom, $E_{Coulomb}\left(MO.atom, msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|>13.605804\ eV$:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|} \tag{15.62}$$

For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|<13.605804\ eV$:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|}{13.605804\ eV} \tag{15.63}$$

(iii) the ratio that is less than one of $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the valence energy, $E(valence)$, of the participating AO or HO of the atom where $E(valence)$ is the ionization energy or $E\left(MO.atom, msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32). For $\left|E(valence)\right|>13.605804\ eV$:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}} = \frac{13.605804\ eV}{\left|E(valence)\right|} \tag{15.64}$$

For $\left|E(valence)\right|<13.605804\ eV$:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{\left|E(valence)\right|}{13.605804\ eV} \tag{15.65}$$

(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom, $E_{Coulomb}\left(MO.atom, msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, $E(valence)$, of the participating AO or HO of a second atom to which the first is energy matched where $E(valence)$ is the

ionization energy or $E\left(MO.atom,msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|>E(valence)$:

$$c_2=\frac{|E(valence)|}{\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|} \tag{15.66}$$

For $\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|<E(valence)$:

$$c_2=\frac{\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|}{|E(valence)|} \tag{15.67}$$

(v) the ratio that is less than one of the magnitude of the valence-level energies, $E_n(valence)$, of the AO or HO of the nth participating atom of two that are energy matched where $E(valence)$ is the ionization energy or $E\left(MO.atom,msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32):

$$c_2=\frac{E_1(valence)}{E_2(valence)} \tag{15.68}$$

(vi) the factor that is the ratio of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.68); alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2=\frac{c_2(1)}{c_2(2)} \tag{15.69}$$

(vii) the factor that is the product of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.69);

alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) \tag{15.70}$$

The hybridization factor c_2 corresponds to the force constant k (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), then C_2 corresponding to k' (Eq. (15.1)) is given by Eqs. (15.62-15.70).

Specific examples of the factors c_2 and C_2 of a H_2-type ellipsoidal MO of Eq. (15.51) given in following sections are

$$c_2(C2sp^3HO\ to\ F) = \frac{E(C,2sp^3)}{E(F)} c_2(C2sp^3HO) = \frac{-14.63489\ eV}{-17.42282\ eV}(0.91771) = 0.77087;$$

$$C_2(C2sp^3HO\ to\ Cl) = \frac{E(Cl)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-12.96764\ eV}{-14.63489\ eV}(0.91771) = 0.81317;$$

$$C_2(C2sp^3HO\ to\ Br) = \frac{E(Br)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-11.81381\ eV}{-14.63489\ eV}(0.91771) = 0.74081;$$

$$C_2(C2sp^3HO\ to\ I) = \frac{E(I)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-10.45126\ eV}{-14.63489\ eV}(0.91771) = 0.65537;$$

$$c_2(C2sp^3HO\ to\ O) = \frac{E(O)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-13.61806\ eV}{-14.63489\ eV}(0.91771) = 0.85395;$$

$$c_2(H\ to\ 1°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.35946\ eV} = 0.94627;$$

$$c_2(C2sp^3HO\ to\ N) = \frac{E(N)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-14.53414\ eV}{-14.63489\ eV}(0.91771) = 0.91140;$$

$$c_2(H\ to\ 2°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.56407\ eV} = 0.93383;$$

$$C_2(S3p\ to\ H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001\ eV}{-13.60580\ eV} = 0.76144;$$

$$C_2(C2sp^3HO\ to\ \mathrm{S}) = \frac{E(S)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-10.36001\ eV}{-14.63489\ eV}(0.91771) = 0.64965;$$

$$c_2\left(O\ to\ S3sp^3\ to\ C2sp^3HO\right)=\frac{E(O)}{E(S)}c_2\left(C2sp^3HO\right)$$
$$=\frac{-13.61806\ eV}{-10.36001\ eV}(0.91771);$$
$$=1.20632$$

$$c_2\left(S3sp^3\right)=\frac{E_{Coulomb}\left(S3sp^3\right)}{E(H)}=\frac{-11.57099\ eV}{-13.60580\ eV}=0.85045;$$

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right)=\frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right)=\frac{-11.52126\ eV}{-14.63489\ eV}(0.85045)=0.66951;$$

$$C_2\left(S3sp^3\ to\ O\ to\ C2sp^3HO\right)=\frac{E\left(S,3sp^3\right)}{E(O,2p)}c_2\left(C2sp^3HO\right)$$
$$=\frac{-11.52126\ eV}{-13.61806\ eV}(0.91771);$$
$$=0.77641$$

$$c_2\left(O\ to\ N2p\ to\ C2sp^3HO\right)=\frac{E(O)}{E(N)}c_2\left(C2sp^3HO\right)$$
$$=\frac{-13.61806\ eV}{-14.53414\ eV}(0.91771);$$
$$=0.85987$$

$$c_2\left(N2p\ to\ O2p\right)=\frac{c_2\left(C2sp^3HO\ to\ N\right)}{c_2\left(C2sp^3HO\ to\ O\right)}=\frac{0.91140}{0.85395}=1.06727;$$

$$C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=\frac{13.605804\ eV}{15.95955\ eV}=0.85252;$$

$$c_2\left(arylC2sp^3HO\ to\ O\right)=\frac{E(O)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)$$
$$=\frac{-13.61806\ eV}{-14.63489\ eV}(0.85252)\quad;$$
$$=0.79329$$

$$c_2\left(H\ to\ \text{anline}\ N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}=\frac{-14.53414\ eV}{-15.76868\ eV}=0.92171;$$

$$c_2\left(arylC2sp^3HO\ to\ N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)$$
$$=\frac{-14.53414\ eV}{-14.63489\ eV}(0.85252)\quad,$$
$$=0.84665$$

and

$$C_2\left(S3p \text{ to aryl-type } C2sp^3HO\right)=\frac{E\left(S,3p\right)}{E\left(C,2sp^3\right)}=\frac{-10.36001\ eV}{-15.76868\ eV}=0.65700\,.$$

MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95) wherein the nucleus of a B atom and the nucleus of a A atom comprise the foci of each H_2-type ellipsoidal MO of an $A-B$ bond. The parameters of the point of intersection of each H_2-type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r=r_0\frac{1+e}{1+e\cos\theta'} \tag{15.71}$$

The radius of the A shell is r_A, and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_A=\left(a-c'\right)\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'} \tag{15.72}$$

The polar angle θ' at the intersection point is given by

$$\theta'=\cos^{-1}\left(\frac{a}{c'}\left(\left(a-c'\right)\frac{1+\frac{c'}{a}}{a_0}-1\right)\right) \tag{15.73}$$

Then, the angle $\theta_{A\,AO}$ the radial vector of the A AO makes with the internuclear axis is

$$\theta_{A\,AO}=180°-\theta' \tag{15.74}$$

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle $\omega t=\theta_{H_2MO}$ between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A\sin\theta_{A\,AO}=b\sin\theta_{H_2MO} \tag{15.75}$$

such that

$$\theta_{H_2MO}=\sin^{-1}\frac{r_a\sin\theta_{A\,AO}}{b} \tag{15.76}$$

The distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \tag{15.77}$$

The distance d_{AAO} along the internuclear axis from the origin of the A atom to the point of intersection of the orbitals is given by

$$d_{AAO} = c' - d_{H_2MO} \tag{15.78}$$

BOND ANGLES

Further consider an ACB MO comprising a linear combination of $C-A$-bond and $C-B$-bond MOs where C is the general central atom. A bond is also possible between the A and B atoms of the $C-A$ and $C-B$ bonds. Such $A-B$ bonding would decrease the $C-A$ and $C-B$ bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the $\angle ACB$ bond angle is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal A and B atoms is zero. The force constant k' of a H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1C_2 2e^2}{4\pi\varepsilon_o} \tag{15.79}$$

where C_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal $A-H$ (A is H or other atom) and 1 otherwise and C_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52). The distance from the origin of the MO to each focus c' of the $A-B$ ellipsoidal MO is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.80}$$

The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.81}$$

The length of the semiminor axis of the prolate spheroidal $A-B$ MO $b=c$ is given by Eq. (15.4).

The component energies and the total energy, $E_T(H_2MO)$, of the $A-B$ bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of H_2 except that the terms based on charge are multiplied by c_{BO}, the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules. The kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by c_1, the fraction of the H_2-type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal $A-H$ (A is H or other atom) and 1 otherwise. The electron energy terms are further multiplied by c_2', the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when $A-B$ comprises atoms other than H, $E_T\left(atom-atom,msp^3.AO\right)$, the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give $E_T(H_2MO)$:

$$E_T(H_2MO)=\frac{-e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T\left(atom-atom,msp^3.AO\right) \quad (15.82)$$

The radiation reaction force in the case of the vibration of $A-B$ in the transition state corresponds to the Doppler energy, E_D, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the $A-B$ MO is given by the sum of $E_T(H_2MO)$ (Eq. (15.82)) and $\bar{E}_{osc}$ given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy $E_T\left(A-B\right)$ of the $A-B$ MO including the Doppler term is

$$E_T\left(A-B\right)=\left[\left(\frac{-e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T\left(atom-atom,msp^3.AO\right)\right)\right]$$
$$\left[\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}}\right]+\frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_1c_2'e^2}{8\pi\varepsilon_o a^3}-\frac{c_{BO}e^2}{8\pi\varepsilon_o\left(a+c'\right)^3}}{\mu}}\right] \quad (15.83)$$

where C_{1o} is the fraction of the H_2-type ellipsoidal MO basis function of the oscillatory transition state of the $A-B$ bond which is 0.75 (Eq. (13.233)) in the case of H bonding to a central atom and 1 otherwise, C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and $\mu=\frac{m_1m_2}{m_1+m_2}$ is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the $A-B$ ellipsoidal MO is zero, $E_T\left(A-B\right)$ given by Eq. (15.83) is set equal to zero. Substitution of Eq. (15.81) into Eq. (15.83) gives

$$0=\left[\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T\left(atom-atom,msp^3.AO\right)\right)\right]$$
$$\left[\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}}\right]+\frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_1c_2'e^2}{8\pi\varepsilon_o a^3}-\frac{c_{BO}e^2}{8\pi\varepsilon_o\left(a+\sqrt{\frac{aa_0}{2C_1C_2}}\right)^3}}{\mu}}\right] \quad (15.84)$$

The vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by

$$f\left(a\right)=-c_{BO}\frac{c_1c_2'e^2}{4\pi\varepsilon_0 a^3} \quad (15.85)$$

and

$$f'(a) = 2c_{BO}\frac{c_1c_2'e^2}{4\pi\varepsilon_0 a^3} \tag{15.86}$$

The nuclear repulsion force and its derivative are given by

$$f(a+c') = \frac{e^2}{8\pi\varepsilon_o(a+c')^2} \tag{15.87}$$

and

$$f'(a+c') = -\frac{e^2}{4\pi\varepsilon_o(a+c')^3} \tag{15.88}$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{c_1c_2'e^2}{4\pi\varepsilon_0 a^3} - \frac{e^2}{8\pi\varepsilon_0(a+c')^2}}{\mu}} \tag{15.89}$$

Since both terms of $\bar{E}_{osc} = \bar{E}_D + \bar{E}_{Kvib}$ are small due to the large values of a and c', to very good approximation, a convenient form of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \left[\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2'\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}} - 1\right] + E_T\left(atom-atom, msp^3.AO\right)\right)\right.$$
$$\left.\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_1e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right] + \frac{1}{2}\hbar\sqrt{\frac{\frac{c_1e^2}{8\pi\varepsilon_o a^3} - \frac{e^2}{8\pi\varepsilon_o\left(a+\sqrt{\frac{aa_0}{2C_1C_2}}\right)^3}}{\mu}}\right] \tag{15.90}$$

From the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the $A-B$ MO can be solved. The most convenient way to solve Eq. (15.90) is by the reiterative technique using a computer.

A factor c_2 of a given atom in the determination of c_2' for calculating the zero of the total $A-B$ bond energy is typically given by Eqs. (15.62-15.65). In the case of a $H-H$ terminal bond of an alkyl or alkenyl group, c_2' is typically the ratio of c_2 of Eq. (15.62) for the $H-H$ bond which is one and c_2 of the carbon of the corresponding $C-H$ bond:

$$c_2' = \frac{1}{c_2(C2sp^3)} = \frac{13.605804\ eV}{E_{Coulomb}\left(C-H\ C2sp^3\right)} \tag{15.91}$$

In the case of the determination of the bond angle of the ACH MO comprising a linear combination of $C-A$-bond and $C-H$-bond MOs where A and C are general, C is the central atom, and c_2 for an atom is given by Eqs. (15.62-15.70), c_2' of the $A-H$ terminal bond is typically the ratio of c_2 of the A atom for the $A-H$ terminal bond and c_2 of the C atom of the corresponding $C-H$ bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3)} \tag{15.92}$$

In the case of the determination of the bond angle of the COH MO of an alcohol comprising a linear combination of $C-O$-bond and $O-H$-bond MOs where C, O, and H are carbon, oxygen, and hydrogen, respectively, c_2' of the $C-H$ terminal bond is typically 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the $C2sp^3$ HO.

In the determination of the hybridization factor c_2' of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy, $E_{Coulomb}\left(MO.atom,msp^3\right)$, or the energy, $E\left(MO.atom,msp^3\right)$, the radius $r_{A-B\ AorBsp^3}$ of the A or B AO or HO of the heteroatom of the $A-B$ terminal bond MO such as the $C2sp^3$ HO of a terminal $C-C$ bond is calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy $E_{Coulomb}\left(MO.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E\left(MO.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(MO.atom,msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

In the specific case of the terminal bonding of two carbon atoms, the c_2 factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy $E_{Coulomb}\left(C-C\ C2sp^3\right)$ of the outer electron of the $C2sp^3$ shell given by Eq. (15.19) with the

radius $r_{C-C\ C2sp^3}$ of each $C2sp^3$ HO of the terminal $C-C$ bond calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, $0.92918\ eV$ (Eq. (14.513)), corresponding to the terminal $C-C$ bond. The corresponding $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.90) is $E_T\left(C-C\ C2sp^3\right)=-1.85836\ eV$.

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus, c_2' is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

$$c_2'=\frac{1}{2}\left(c_2'\left(atom\ 1\right)+c_2'\left(atom\ 2\right)\right) \tag{15.93}$$

In the exemplary cases of $C-C$, $O-O$, and $N-N$ where C is carbon:

$$\begin{aligned} c_2' &= \frac{1}{2}\left(\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-A\ A_1AO/HO}}}+\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-A\ A_2AO/HO}}}\right) \\ &= \frac{1}{2}\left(\frac{13.605804\ eV}{E_{Coulomb}\left(A-A.A_1AO/HO\right)}+\frac{13.605804\ eV}{E_{Coulomb}\left(A-A.A_2AO/HO\right)}\right) \end{aligned} \tag{15.94}$$

In the exemplary cases of $C-N$, $C-O$, and $C-S$,

$$c_2'=\frac{1}{2}\left(\frac{13.605804\ eV}{E_{Coulomb}\left(C-B\ C2sp^3\right)}+c_2\left(C\ to\ B\right)\right) \tag{15.95}$$

where C is carbon and $c_2\left(C\ to\ B\right)$ is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom B to that of the atom C in the group. For these cases, the corresponding $E_T\left(atom-atom,msp^3.AO\right)$ term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

$E_T\left(C-O\ C2sp^3.O2p\right)=-1.44915\ eV$; $E_T\left(C-O\ C2sp^3.O2p\right)=-1.65376\ eV$;

$E_T\left(C-N\ C2sp^3.N2p\right)=-1.44915\ eV$; $E_T\left(C-S\ C2sp^3.S2p\right)=-0.72457\ eV$;

$E_T\left(O-O\ O2p.O2p\right)=-1.44915\ eV$; $E_T\left(O-O\ O2p.O2p\right)=-1.65376\ eV$;

$E_T\left(N-N\ N2p.N2p\right)=-1.44915\ eV$; $E_T\left(N-O\ N2p.O2p\right)=-1.44915\ eV$;

$E_T\left(F-F\ F2p.F2p\right)=-1.44915\ eV$; $E_T\left(Cl-Cl\ Cl3p.Cl3p\right)=-0.92918\ eV$;

$E_T\left(Br-Br\ Br4p.Br4p\right)=-0.92918\ eV$; $E_T\left(I-I\ I5p.I5p\right)=-0.36229\ eV$;

$E_T\left(C-F\ C2sp^3.F2p\right)=-1.85836\ eV$; $E_T\left(C-Cl\ C2sp^3.Cl3p\right)=-0.92918\ eV$;

$E_T\left(C-Br\ C2sp^3.Br4p\right)=-0.72457\ eV$; $E_T\left(C-I\ C2sp^3.I5p\right)=-0.36228\ eV$, and

$E_T\left(O-Cl\ O2p.Cl3p\right)=-0.92918\ eV$.

In the case that the terminal bond is $X-X$ where X is a halogen atom, c_1 is one, and c_2' is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where $E_{Coulomb}\left(MO.atom,msp^3\right)$ is determined using Eq. (15.32) and $E_{Coulomb}\left(MO.atom,msp^3\right)=13.605804\ eV$ for $X=I$. The factor C_1 of Eq. (15.90) is one for all halogen atoms. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2\left(1\right)$ being that of the halogen given by Eq. (15.68) that matches the valence energy of X ($E_1\left(valence\right)$) to that of the $C2sp^3$ HO ($E_2\left(valence\right)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2\left(2\right)=0.91771$, Eq. (13.430)). $E_T\left(atom-atom,msp^3.AO\right)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.44915\ eV$, $-0.92918\ eV$, $-0.92918\ eV$, and $-0.33582\ eV$ for F, Cl, Br, and I, respectively.

Consider the case that the terminal bond is $C-X$ where C is a carbon atom and X is a halogen atom. The factors c_1 and C_1 of Eq. (15.90) are one for all halogen atoms. For $X=F$, c_2' is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and F atoms where c_2 for carbon is given by Eq. (15.62) and c_2 for fluorine matched to carbon is given by Eq. (15.70) with $c_2\left(1\right)$ for the fluorine atom given by Eq. (15.68) that matches the valence energy of F ($E_1\left(valence\right)=-17.42282\ eV$) to that of the $C2sp^3$ HO

($E_2(valence) = -14.63489\,eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2) = 0.91771$, Eq. (13.430)). The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\,eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, c_2' is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom. C_2 of the terminal-atom bond matches that used to determine the energies of the corresponding $C-X$-bond MO. Then, C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2(1)$ for the halogen atom given by Eq. (15.68) that matches the valence energy of X ($E_1(valence)$) to that of the $C2sp^3$ HO ($E_2(valence) = -14.63489\,eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2) = 0.91771$, Eq. (13.430)). $E_T(atom-atom, msp^3.AO)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.85836\,eV$, $-0.92918\,eV$, $-0.72457\,eV$, and $-0.33582\,eV$ for F, Cl, Br, and I, respectively.

Consider the case that the terminal bond is $H-X$ corresponding to the angle of the atoms HCX where C is a carbon atom and X is a halogen atom. The factors c_1 and C_1 of Eq. (15.90) are 0.75 for all halogen atoms. For $X = F$, c_2' is given by Eq. (15.69) with c_2 of the participating carbon and F atoms given by Eq. (15.62) and Eq. (15.65), respectively. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\,eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, c_2' is also given by Eq. (15.69) with c_2 of the participating carbon given by Eq. (15.62) and c_2 of the participating X atom given by $c_2 = 0.91771$ (Eq. (13.430)) since the X atom is energy matched to the $C2sp^3$ HO. In these cases, C_2 is given by Eq. (15.65) for the corresponding atom X where C_2 matches the energy of the atom X to that of H.

Using the distance between the two atoms A and B of the general molecular group ACB when the total energy of the corresponding $A-B$ MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1 s_2 \text{cosine}\theta = s_3^2 \tag{15.96}$$

With $s_1 = 2c'_{C-A}$, the internuclear distance of the $C-A$ bond, $s_2 = 2c'_{C-B}$, the internuclear distance of each $C-B$ bond, and $s_3 = 2c'_{A-B}$, the internuclear distance of the two terminal atoms, the bond angle $\theta_{\angle ACB}$ between the $C-A$ and $C-B$ bonds is given by

$$\left(2c'_{C-A}\right)^2 + \left(2c'_{C-B}\right)^2 - 2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)\text{cosine}\,\theta = \left(2c'_{A-B}\right)^2 \tag{15.97}$$

$$\theta_{\angle ACB} = \cos^{-1}\left(\frac{\left(2c'_{C-A}\right)^2 + \left(2c'_{C-B}\right)^2 - \left(2c'_{A-B}\right)^2}{2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)}\right) \tag{15.98}$$

Consider the exemplary structure $C_bC_a(O_a)O_b$ wherein C_a is bound to C_b, O_a, and O_b. In the general case that the three bonds are coplanar and two of the angles are known, say θ_1 and θ_2, then the third θ_3 can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \tag{15.99}$$

In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say θ_1, then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{\left(360 - \theta_1\right)}{2} \tag{15.100}$$

ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES TRIANGLE

In the general case where the group comprises three $A-B$ bonds having B as the central atom at the apex of a pyramidal structure formed by the three bonds with the A atoms at the base in the xy-plane. The C_{3v} axis centered on B is defined as the vertical or z-axis, and any two $A-B$ bonds form an isosceles triangle. Then, the angle of the bonds and the distances from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance $d_{origin-B}$ from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60°} \tag{15.101}$$

the height along the z-axis from the origin to the A nucleus d_{height} is given by

$$d_{height} = \sqrt{\left(2c'_{A-B}\right)^2 - \left(d_{origin-B}\right)^2}\text{, and} \tag{15.102}$$

the angle θ_v of each $A-B$ bond from the z-axis is given by

$$\theta_v = \tan^{-1}\left(\frac{d_{origin-B}}{d_{height}}\right) \tag{15.103}$$

Consider the case where the central atom B is further bound to a fourth atom C and the $B-C$ bond is along the z-axis. Then, the bond $\theta_{\angle ABC}$ given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_v \tag{15.104}$$

DIHEDRAL ANGLE

Consider the plane defined by a general ACA MO comprising a linear combination of two $C-A$-bond MOs where C is the central atom. The dihedral angle $\theta_{\angle BC/ACA}$ between the ACA-plane and a line defined by a third bond with C, specifically that corresponding to a $C-B$-bond MO, is calculated from the bond angle $\theta_{\angle ACA}$ and the distances between the A, B, and C atoms. The distance d_1 along the bisector of $\theta_{\angle ACA}$ from C to the internuclear-distance line between A and A, $2c'_{A-A}$, is given by

$$d_1 = 2c'_{C-A}\cos\frac{\theta_{\angle ACA}}{2} \tag{15.105}$$

where $2c'_{C-A}$ is the internuclear distance between A and C. The atoms A, A, and B define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle ABA}$ can be solved from the internuclear distances between A and A, $2c'_{A-A}$, and between A and B, $2c'_{A-B}$, using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1}\left(\frac{\left(2c'_{A-B}\right)^2 + \left(2c'_{A-B}\right)^2 - \left(2c'_{A-A}\right)^2}{2\left(2c'_{A-B}\right)\left(2c'_{A-B}\right)}\right) \tag{15.106}$$

Then, the distance d_2 along the bisector of $\theta_{\angle ABA}$ from B to the internuclear-distance line $2c'_{A-A}$, is given by

$$d_2 = 2c'_{A-B}\cos\frac{\theta_{\angle ABA}}{2} \tag{15.107}$$

The lengths d_1, d_2, and $2c'_{C-B}$ define a triangle wherein the angle between d_1 and the internuclear distance between B and C, $2c'_{C-B}$, is the dihedral angle $\theta_{\angle BC/ACA}$ that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1}\left(\frac{d_1^2 + \left(2c'_{C-B}\right)^2 - d_2^2}{2d_1\left(2c'_{B-C}\right)}\right) \tag{15.108}$$

SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitsphere solutions bridged by molecular orbitals comprised of the H_2-type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy E_{mag} (e.g. given by Eq. (15.58)) for a $C2sp^3$ HO and Eq.(15.59) for an $O2p$ AO) was subtracted for each set of unpaired electrons created by bond breakage.

The bond energy is not equal to the component energy of each bond as it exists in the molecule; although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will effect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and $E\left(C,2sp^3\right) = -14.63489\ eV$ (Eq. (13.428)). The intercept angles are determined from Eqs.

(15.71-15.78) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple H_2-type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule (C_6H_6) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

C_6H_6 can be considered a linear combination of three ethylene molecules wherein a $C-H$ bond of each CH_2 group of $H_2C=CH_2$ is replaced by a $C=C$ bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. The radius $r_{ethylene2sp^3}$ ($0.85252a_0$) of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ ($-15.95955\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E\left(C_{ethylene},2sp^3\right)$ ($-15.76868\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.246). $E_T\left(C=C,2sp^3\right)$ ($-1.13380\ eV$) (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between $E\left(C_{ethylene},2sp^3\right)$ and $E\left(C,2sp^3\right)$. C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each $2sp^3$ HO of each carbon atom initially has four unpaired electrons. Thus, the $6\,H$ atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3-hybridized carbon atoms contribute twenty-four electrons to form six $C-H$ bonds and six $C=C$ bonds. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. Each $C=C$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ and each $C=C$ bond comprises a linear combination of one and two diatomic H_2-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of $C=C$-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\begin{cases} 3\left(2\ C2sp^3+0.75\ H_2\ MO\right)\rightarrow 3\left(\overset{4e}{C=C}\right)-ethylene-type-bond\ MO \\ \rightarrow 6\left(\overset{3e}{C=C}\right)-bond\ MO\ of\ benzene \end{cases} \tag{15.142}$$

The linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond $C=C$-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the $C=C$-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each $C=C$-bond gives rise to the $C_{benzene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and C_2 of Eq. (15.42) for the aromatic $\overset{3e}{C=C}$-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=\frac{13.605804\ eV}{15.95955\ eV}=0.85252 \tag{15.143}$$

The energies of each $\overset{3e}{C=C}$ bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the $\overset{3e}{C=C}$ bonding of benzene wherein each of the six $\overset{3e}{C=C}$ bonds of benzene comprises $(0.75)(4)=3$ electrons according to Eq. (15.142). The total energy of the bonds of the eighteen electrons of the $\overset{3e}{C=C}$ bonds of benzene, $E_T\left(C_6H_6,\overset{3e}{C=C}\right)$, is given by $(6)(0.75)$ times $E_{T+osc}(C=C)$ (Eq. (14.492)), the total energy of the $\overset{3e}{C=C}$-bond MO of benzene including the Doppler term, minus eighteen times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the $\overset{3e}{C=C}$ bonds of bond order two. Thus, the total energy of the six $\overset{3e}{C=C}$ bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned}E_T\left(C_6H_6,\overset{3e}{C=C}\right)&=(6)(0.75)E_{T+osc}(C=C)-(6)(3)E\left(C,2sp^3\right)\\&=(6)(0.75)(-66.05796\ eV)-18(-14.63489\ eV)\\&=-297.26081\ eV-(-263.42798\ eV)\\&=-33.83284\ eV\end{aligned} \tag{15.144}$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds. E_{hv} of an aromatic bond is given by $E_T\left(H_2\right)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_2-type MO such that

$$\overline{E}_{osc}=n_1\left(\overline{E}_D+\overline{E}_{Kvib}\right)=n_1\left(-31.63536831\ eV\sqrt{\frac{2\overline{E}_K}{Mc^2}}+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.145}$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56). Multiplication of

the total energy given by Eq. (15.55) by $f_1 = 0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_T(Group) = f_1\left(\begin{array}{l} E(basis\ energies) + E_T\left(atom - atom, msp^3.AO\right) \\ -31.63536831\ eV\sqrt{\dfrac{2\hbar\sqrt{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}} + n_1\bar{E}_{Kvib} + c_3\dfrac{8\pi\mu_o\mu_B^2}{r^3} \end{array}\right) \quad (15.146)$$

The total bond energy of the aromatic group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of $c_4 E_{initial}\left(c_4\ AO/HO\right)$ and $c_5 E_{initial}\left(c_5\ AO/HO\right)$:

$$E_D(Group) = -\left(\begin{array}{l} f_1\left(\begin{array}{l} E(basis\ energies) + E_T\left(atom - atom, msp^3.AO\right) \\ -31.63536831\ eV\sqrt{\dfrac{2\hbar\sqrt{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}} + n_1\bar{E}_{Kvib} + c_3\dfrac{8\pi\mu_o\mu_B^2}{r^3} \end{array}\right) \\ -\left(c_4 E_{initial}\left(AO/HO\right) + c_5 E_{initial}\left(c_5\ AO/HO\right)\right) \end{array}\right) \quad (15.147)$$

Since there are three electrons per aromatic bond, c_4 is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule (C_6H_6) section. The energy components of V_e, V_p, T, V_m, and E_T are the same as those of the hydrogen carbide radical, except that $E_T\left(C = C, 2sp^3\right) = -1.13379\ eV$ (Eq. (14.247)) is subtracted from $E_T(CH)$ of Eq. (13.495) to match the energy of each $C-H$-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T\left(atom - atom, msp^3.AO\right) = -1.13379\ eV$.

The total energy of the benzene $C-H$-bond MO, $E_{T_{benzene}}\left(C-H\right)$, given by Eq. (14.467) is the sum of $0.5E_T\left(C = C, 2sp^3\right)$, the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the formation of the corresponding $C\overset{3e}{=}C$-bond MO (Eq. (14.247)), and $E_{T_{benzene}}(CH)$, the σ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_1 = 1$ and $E_T\left(atom - atom, msp^3.AO\right) = \dfrac{-1.13379\ eV}{2}$. Thus, the energy

contribution to the single aromatic CH bond is one half that of the $\overset{3e}{C=C}$ double bond contribution. This matches the energies of the CH and $\overset{3e}{C=C}$ aromatic groups, conserves the electron number with the equivalent charge density as that of $s=1$ in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic $\overset{3e}{C=C}$ bonds to give CH groups creates unpaired electrons in these fragments that corresponds to $c_3=1$ in Eq. (15.56) with E_{mag} given by Eq. (15.58).

Each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each $C-H$ bond, $-E_{D_{benzene}}\left({}^{12}CH\right)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T\left(C_6H_6,C-H\right)$, given by Eq. (14.494) is

$$E_T\left(C_6H_6,C-H\right)=(6)\left(-E_{D_{benzene}}\left({}^{12}CH\right)\right)=6\left(-3.90454\ eV\right)=-23.42724\ eV \tag{15.148}$$

The total bond dissociation energy of benzene, $E_D\left(C_6H_6\right)$, given by Eq. (14.495) is the negative sum of $E_T\left(C_6H_6,\overset{3e}{C=C}\right)$ (Eq. (14.493)) and $E_T\left(C_6H_6,C-H\right)$ (Eq. (14.494)):

$$\begin{aligned} E_D\left(C_6H_6\right) &= -\left(E_T\left(C_6H_6,\overset{3e}{C=C}\right)+E_T\left(C_6H_6,C-H\right)\right) \\ &= -\left(\left(-33.83284\ eV\right)+\left(-23.42724\ eV\right)\right) \\ &= 57.2601\ eV \end{aligned} \tag{15.149}$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each $E_D\left(_{Group}\right)$ of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH (i)

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and experimental values [1].

Parameter	$C^{3e}=C$ Group	CH Group
$a\ (a_0)$	1.47348	1.60061
$c'\ (a_0)$	1.31468	1.03299
Bond Length $2c'$ (□)	1.39140	1.09327
Exp. Bond Length (□)	1.399 (benzene)	1.101 (benzene)
$b,c\ (a_0)$	0.66540	1.22265
e	0.89223	0.64537

Table 15.216. The energy parameters (eV) of functional groups of aromatics and heterocyclics.

Parameters	$C^{3e}=C$ Group	CH Group
f_1	0.75	1
n_1	2	1
n_2	0	0
n_3	0	0
C_1	0.5	0.75
C_2	0.85252	1
c_1	1	1
c_2	0.85252	0.91771
c_3	0	1
c_4	3	1
c_5	0	1
C_{1o}	0.5	0.75
C_{2o}	0.85252	1
$V_e\ (eV)$	-101.12679	-37.10024
$V_p\ (eV)$	20.69825	13.17125
$T\ (eV)$	34.31559	11.58941
$V_m\ (eV)$	-17.15779	-5.79470
$E_{(AO/HO)}\ (eV)$	0	-14.63489
$\Delta E_{H_2MO\ (AO/HO)}\ (eV)$	0	-1.13379

$E_T\left(AO/HO\right)(eV)$	0	-13.50110
$E_T\left(H_2MO\right)(eV)$	-63.27075	-31.63539
$E_T\left(atom-atom, msp^3.AO\right)(eV)$	-2.26759	-0.56690
$E_T\left(MO\right)(eV)$	-65.53833	-32.20226
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826
$E_K\ (eV)$	32.73133	17.43132
$\overline{E}_D\ (eV)$	-0.35806	-0.26130
$\overline{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)
$\overline{E}_{osc}\ (eV)$	-0.25982	-0.08364
$E_{mag}\ (eV)$	0.14803	0.14803
$E_T\left(Group\right)(eV)$	-49.54347	-32.28590
$E_{initial}\left(c_4\ AO/HO\right)(eV)$	-14.63489	-14.63489
$E_{initial}\left(c_5\ AO/HO\right)(eV)$	0	-13.59844
$E_D\left(Group\right)(eV)$	5.63881	3.90454

Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)
$C-H\ (CH)$	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597
$\overset{3e}{C}=HC_a-\overset{3e}{C}$	C_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597

Bond	$E_{Coulomb}\left(C2sp^3\right)$(eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (CH)$	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\overset{3e}{C}=HC_a-\overset{3e}{C}$	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Formula	Name	$\overset{3e}{C}=C$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6	Benzene	6	6	57.26008	57.26340	0.00006

Table 15.218. The bond angle parameters of benzene and experimental values [1]. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1
$\angle CCH$ (aromatic)											

Atoms of Angle	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)					120.19		119.91	120 [50-52] (benzene)

Table 1.1. The calculated and experimental total bond energies of n-alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_8	Propane	41.46896	41.434	-0.00085
C_4H_{10}	Butane	53.62666	53.61	-0.00036
C_5H_{12}	Pentane	65.78436	65.77	-0.00017
C_6H_{14}	Hexane	77.94206	77.93	-0.00019
C_7H_{16}	Heptane	90.09976	90.09	-0.00013
C_8H_{18}	Octane	102.25746	102.25	-0.00006
C_9H_{20}	Nonane	114.41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	126.57286	126.57	-0.00003
$C_{11}H_{24}$	Undecane	138.73056	138.736	0.00004
$C_{12}H_{26}$	Dodecane	150.88826	150.88	-0.00008
$C_{18}H_{38}$	Octadecane	223.83446	223.85	0.00008

Table 1.2. The calculated and experimental total bond energies of branched alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_{10}	Isobutane	53.69922	53.695	-0.00007
C_5H_{12}	Isopentane	65.85692	65.843	-0.00021
C_5H_{12}	Neopentane	65.86336	65.992	0.00195
C_6H_{14}	2-Methylpentane	78.01462	78.007	-0.00010
C_6H_{14}	3-Methylpentane	78.01462	77.979	-0.00046
C_6H_{14}	2,2-Dimethylbutane	78.02106	78.124	0.00132
C_6H_{14}	2,3-Dimethylbutane	77.99581	78.043	0.00061
C_7H_{16}	2-Methylhexane	90.17232	90.160	-0.00014
C_7H_{16}	3-Methylhexane	90.17232	90.127	-0.00051
C_7H_{16}	3-Ethylpentane	90.17232	90.108	-0.00072
C_7H_{16}	2,2-Dimethylpentane	90.17876	90.276	0.00107
C_7H_{16}	2,2,3-Trimethylbutane	90.22301	90.262	0.00044
C_7H_{16}	2,4-Dimethylpentane	90.24488	90.233	-0.00013
C_7H_{16}	3,3-Dimethylpentane	90.17876	90.227	0.00054
C_8H_{18}	2-Methylheptane	102.33002	102.322	-0.00008
C_8H_{18}	3-Methylheptane	102.33002	102.293	-0.00036
C_8H_{18}	4-Methylheptane	102.33002	102.286	-0.00043
C_8H_{18}	3-Ethylhexane	102.30169	102.274	-0.00027
C_8H_{18}	2,2-Dimethylhexane	102.33646	102.417	0.00079
C_8H_{18}	2,3-Dimethylhexane	102.31121	102.306	-0.00005
C_8H_{18}	2,4-Dimethylhexane	102.40258	102.362	-0.00040
C_8H_{18}	2,5-Dimethylhexane	102.40258	102.396	-0.00006
C_8H_{18}	3,3-Dimethylhexane	102.33646	102.369	0.00032
C_8H_{18}	3,4-Dimethylhexane	102.31121	102.296	-0.00015
C_8H_{18}	3-Ethyl-2-methylpentane	102.31121	102.277	-0.00033
C_8H_{18}	3-Ethyl-3-methylpentane	102.33646	102.317	-0.00019
C_8H_{18}	2,2,3-Trimethylpentane	102.38071	102.370	-0.00010
C_8H_{18}	2,2,4-Trimethylpentane	102.40902	102.412	0.00003
C_8H_{18}	2,3,3-Trimethylpentane	102.38071	102.332	-0.00048
C_8H_{18}	2,3,4-Trimethylpentane	102.29240	102.342	0.00049
C_8H_{18}	2,2,3,3-Tetramethylbutane	102.41632	102.433	0.00016
C_9H_{20}	2,3,5-Trimethylhexane	114.54147	114.551	0.00008
C_9H_{20}	3,3-Diethylpentane	114.49416	114.455	-0.00034
C_9H_{20}	2,2,3,3-Tetramethylpentane	114.57402	114.494	-0.00070
C_9H_{20}	2,2,3,4-Tetramethylpentane	114.51960	114.492	-0.00024

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_9H_{20}	2,2,4,4-Tetramethylpentane	114.57316	114.541	-0.00028
C_9H_{20}	2,3,3,4-Tetramethylpentane	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	126.64542	126.680	0.00027
$C_{10}H_{22}$	5-Methylnonane	126.64542	126.663	0.00014

Table 1.3. The calculated and experimental total bond energies of alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6	Propene	35.56033	35.63207	0.00201
C_4H_8	1-Butene	47.71803	47.78477	0.00140
C_4H_8	trans-2-Butene	47.93116	47.90395	-0.00057
C_4H_8	Isobutene	47.90314	47.96096	0.00121
C_5H_{10}	1-Pentene	59.87573	59.95094	0.00125
C_5H_{10}	trans-2-Pentene	60.08886	60.06287	-0.00043
C_5H_{10}	2-Methyl-1-butene	60.06084	60.09707	0.00060
C_5H_{10}	2-Methyl-2-butene	60.21433	60.16444	-0.00083
C_5H_{10}	3-Methyl-1-butene	59.97662	60.01727	0.00068
C_6H_{12}	1-Hexene	72.03343	72.12954	0.00133
C_6H_{12}	trans-2-Hexene	72.24656	72.23733	-0.00013
C_6H_{12}	trans-3-Hexene	72.24656	72.24251	-0.00006
C_6H_{12}	2-Methyl-1-pentene	72.21854	72.29433	0.00105
C_6H_{12}	2-Methyl-2-pentene	72.37203	72.37206	0.00000
C_6H_{12}	3-Methyl-1-pentene	72.13432	72.19173	0.00080
C_6H_{12}	4-Methyl-1-pentene	72.10599	72.21038	0.00145
C_6H_{12}	3-Methyl-trans-2-pentene	72.37203	72.33268	-0.00054
C_6H_{12}	4-Methyl-trans-2-pentene	72.34745	72.31610	-0.00043
C_6H_{12}	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C_6H_{12}	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C_6H_{12}	3,3-Dimethyl-1-butene	72.31796	72.30366	-0.00020
C_6H_{12}	2,3-Dimethyl-2-butene	72.49750	72.38450	-0.00156
C_7H_{14}	1-Heptene	84.19113	84.27084	0.00095
C_7H_{14}	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C_7H_{14}	trans-3-Methyl-3-hexene	84.52973	84.42112	-0.00129
C_7H_{14}	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C_7H_{14}	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C_7H_{14}	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102
C_7H_{14}	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C_7H_{14}	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C_7H_{14}	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C_8H_{16}	1-Octene	96.34883	96.41421	0.00068
C_8H_{16}	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C_8H_{16}	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C_8H_{16}	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C_8H_{16}	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	193.61043	193.71766	0.00055

Table 1.4. The calculated and experimental total bond energies of alkynes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_4	Propyne	29.42932	29.40432	-0.00085
C_4H_6	1-Butyne	41.58702	41.55495	-0.00077
C_4H_6	2-Butyne	41.72765	41.75705	0.00070
C_9H_{16}	1-Nonyne	102.37552	102.35367	-0.00021

Table 1.5. The calculated and experimental total bond energies of alkyl fluorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF_4	Tetrafluoromethane	21.07992	21.016	-0.00303
CHF_3	Trifluoromethane	19.28398	19.362	0.00405
CH_2F_2	Difluoromethane	18.22209	18.280	0.00314
C_3H_7F	1-Fluoropropane	41.86745	41.885	0.00041
C_3H_7F	2-Fluoropropane	41.96834	41.963	-0.00012

Table 1.6. The calculated and experimental total bond energies of alkyl chlorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CCl_4	Tetrachloromethane	13.43181	13.448	0.00123
$CHCl_3$	Trichloromethane	14.49146	14.523	0.00217
CH_2Cl_2	Dichloromethane	15.37248	15.450	0.00499
CH_3Cl	Chloromethane	16.26302	16.312	0.00299
C_2H_5Cl	Chloroethane	28.61064	28.571	-0.00138
C_3H_7Cl	1-Chloropropane	40.76834	40.723	-0.00112
C_3H_7Cl	2-Chloropropane	40.86923	40.858	-0.00028
C_4H_9Cl	1-Chlorobutane	52.92604	52.903	-0.00044
C_4H_9Cl	2-Chlorobutane	53.02693	52.972	-0.00104
C_4H_9Cl	1-Chloro-2-methylpropane	52.99860	52.953	-0.00085
C_4H_9Cl	2-Chloro-2-methylpropane	53.21057	53.191	-0.00037
$C_5H_{11}Cl$	1-Chloropentane	65.08374	65.061	-0.00034
$C_5H_{11}Cl$	1-Chloro-3-methylbutane	65.15630	65.111	-0.00069
$C_5H_{11}Cl$	2-Chloro-2-methylbutane	65.36827	65.344	-0.00037
$C_5H_{11}Cl$	2-Chloro-3-methylbutane	65.16582	65.167	0.00002
$C_6H_{13}Cl$	2-Chlorohexane	77.34233	77.313	-0.00038
$C_8H_{17}Cl$	1-Chlorooctane	101.55684	101.564	0.00007
$C_{12}H_{25}Cl$	1-Chlorododecane	150.18764	150.202	0.00009
$C_{18}H_{37}Cl$	1-Chlorooctadecane	223.13384	223.175	0.00018

Table 1.7. The calculated and experimental total bond energies of alkyl bromides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CBr_4	Tetrabromomethane	11.25929	11.196	-0.00566
$CHBr_3$	Tribromomethane	12.87698	12.919	0.00323
CH_3Br	Bromomethane	15.67551	15.732	0.00360
C_2H_5Br	Bromoethane	28.03939	27.953	-0.00308
C_3H_7Br	1-Bromopropane	40.19709	40.160	-0.00093
C_3H_7Br	2-Bromopropane	40.29798	40.288	-0.00024
$C_5H_{10}Br_2$	2,3-Dibromo-2-methylbutane	63.48143	63.477	-0.00007
$C_6H_{13}Br$	1-Bromohexane	76.67019	76.634	-0.00047
$C_7H_{15}Br$	1-Bromoheptane	88.82789	88.783	-0.00051
$C_8H_{17}Br$	1-Bromooctane	100.98559	100.952	-0.00033
$C_{12}H_{25}Br$	1-Bromododecane	149.61639	149.573	-0.00029
$C_{16}H_{33}Br$	1-Bromohexadecane	198.24719	198.192	-0.00028

Table 1.8. The calculated and experimental total bond energies of alkyl iodides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CHI_3	Triiodomethane	10.35888	10.405	0.00444
CH_2I_2	Diiodomethane	12.94614	12.921	-0.00195
CH_3I	Iodomethane	15.20294	15.163	-0.00263
C_2H_5I	Iodoethane	27.36064	27.343	-0.00066
C_3H_7I	1-Iodopropane	39.51834	39.516	-0.00006
C_3H_7I	2-Iodopropane	39.61923	39.623	0.00009
C_4H_9I	2-Iodo-2-methylpropane	51.96057	51.899	-0.00119

Table 1.9. The calculated and experimental total bond energies of alkene halides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3Cl	Chloroethene	22.46700	22.505	0.00170
C_3H_5Cl	2-Chloropropene	35.02984	35.05482	0.00071

Table 1.10. The calculated and experimental total bond energies of alcohols using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4O	Methanol	21.11038	21.131	0.00097
C_2H_6O	Ethanol	33.40563	33.428	0.00066
C_3H_8O	1-Propanol	45.56333	45.584	0.00046
C_3H_8O	2-Propanol	45.72088	45.766	0.00098
$C_4H_{10}O$	1-Butanol	57.72103	57.736	0.00026
$C_4H_{10}O$	2-Butanol	57.87858	57.922	0.00074
$C_4H_{10}O$	2-Methyl-1-propananol	57.79359	57.828	0.00060
$C_4H_{10}O$	2-Methyl-2-propananol	58.15359	58.126	-0.00048
$C_5H_{12}O$	1-Pentanol	69.87873	69.887	0.00011

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_5H_{12}O$	2-Pentanol	70.03628	70.057	0.00029
$C_5H_{12}O$	3-Pentanol	70.03628	70.097	0.00087
$C_5H_{12}O$	2-Methyl-1-butananol	69.95129	69.957	0.00008
$C_5H_{12}O$	3-Methyl-1-butananol	69.95129	69.950	-0.00002
$C_5H_{12}O$	2-Methyl-2-butananol	70.31129	70.246	-0.00092
$C_5H_{12}O$	3-Methyl-2-butananol	69.96081	70.083	0.00174
$C_6H_{14}O$	1-Hexanol	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	82.19398	82.236	0.00052
$C_7H_{16}O$	1-Heptanol	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	106.42439	106.459	0.00032
$C_9H_{20}O$	1-Nonanol	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	154.98263	154.984	0.00001
$C_{16}H_{34}O$	1-Hexadecanol	203.61343	203.603	-0.00005

Table 1.11. The calculated and experimental total bond energies of ethers using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6O	Dimethyl ether	32.84496	32.902	0.00174
C_3H_8O	Ethyl methyl ether	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	57.45569	57.499	0.00075
$C_6H_{14}O$	Dipropyl ether	81.86464	81.817	-0.00059
$C_6H_{14}O$	Disopropyl ether	82.06642	82.088	0.00026
$C_6H_{14}O$	t-Butyl ethyl ether	82.10276	82.033	-0.00085
$C_7H_{16}O$	t-Butyl isopropyl ether	94.36135	94.438	0.00081
$C_8H_{18}O$	Dibutyl ether	106.18004	106.122	-0.00055
$C_8H_{18}O$	Di-sec-butyl ether	106.38182	106.410	0.00027
$C_8H_{18}O$	Di-t-butyl ether	106.36022	106.425	0.00061
$C_8H_{18}O$	t-Butyl isobutyl ether	106.65628	106.497	-0.00218

Table 1.12. The calculated and experimental total bond energies of 1° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_5N	Methylamine	23.88297	23.857	-0.00110
C_2H_7N	Ethylamine	36.04067	36.062	0.00060
C_3H_9N	Propylamine	48.19837	48.243	0.00092
$C_4H_{11}N$	Butylamine	60.35607	60.415	0.00098
$C_4H_{11}N$	sec-Butylamine	60.45696	60.547	0.00148
$C_4H_{11}N$	t-Butylamine	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	60.42863	60.486	0.00094

Table 1.13. The calculated and experimental total bond energies of 2° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_7N	Dimethylamine	35.76895	35.765	-0.00012
$C_4H_{11}N$	Diethylamine	60.22930	60.211	-0.00030
$C_6H_{15}N$	Dipropylamine	84.54470	84.558	0.00016
$C_6H_{15}N$	Diisopropylamine	84.74648	84.846	0.00117
$C_8H_{19}N$	Dibutylamine	108.86010	108.872	0.00011
$C_8H_{19}N$	Diisobutylamine	109.00522	109.106	0.00092

Table 1.14. The calculated and experimental total bond energies of 3° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_9N	Trimethylamine	47.83338	47.761	-0.00152
$C_6H_{15}N$	Triethylamine	84.30648	84.316	0.00012
$C_9H_{21}N$	Tripropylamine	120.77958	120.864	0.00070

Table 1.15. The calculated and experimental total bond energies of aldehydes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O	Formaldehyde	15.64628	15.655	0.00056
C_2H_4O	Acetaldehyde	28.18711	28.198	0.00039
C_3H_6O	Propanal	40.34481	40.345	0.00000
C_4H_8O	Butanal	52.50251	52.491	-0.00022
C_4H_8O	Isobutanal	52.60340	52.604	0.00001
$C_5H_{10}O$	Pentanal	64.66021	64.682	0.00034
$C_7H_{14}O$	Heptanal	88.97561	88.942	-0.00038
$C_8H_{16}O$	Octanal	101.13331	101.179	0.00045
$C_8H_{16}O$	2-Ethylhexanal	101.20587	101.259	0.00053

Table 1.16. The calculated and experimental total bond energies of ketones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6O	Acetone	40.68472	40.672	-0.00031
C_4H_8O	2-Butanone	52.84242	52.84	-0.00005
$C_5H_{10}O$	2-Pentanone	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Pentanone	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Methyl-2-butanone	65.10101	65.036	-0.00099
$C_6H_{12}O$	2-Hexanone	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	77.15782	77.138	-0.00025
$C_6H_{12}O$	2-Methyl-3-pentanone	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	77.29432	77.273	-0.00028
$C_7H_{14}O$	3-Heptanone	89.31552	89.287	-0.00032
$C_7H_{14}O$	4-Heptanone	89.31552	89.299	-0.00018
$C_7H_{14}O$	2,2-Dimethyl-3-pentanone	89.45202	89.458	0.00007

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_7H_{14}O$	2,4-Dimethyl-3-pentanone	89.51730	89.434	-0.00093
$C_8H_{16}O$	2,2,4-Trimethyl-3-pentanone	101.71061	101.660	-0.00049
$C_9H_{18}O$	2-Nonanone	113.63092	113.632	0.00001
$C_9H_{18}O$	5-Nonanone	113.63092	113.675	0.00039
$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	113.77604	113.807	0.00027

Table 1.17. The calculated and experimental total bond energies of carboxylic acids using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O_2	Formic acid	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	33.55916	33.537	-0.00066
$C_3H_6O_2$	Propanoic acid	45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	70.03226	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	252.39776	252.514	0.00046

Table 1.18. The calculated and experimental total bond energies of carboxylic acid esters using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_4O_2$	Methyl formate	32.71076	32.762	0.00156
$C_3H_6O_2$	Methyl acetate	45.24849	45.288	0.00087
$C_6H_{12}O_2$	Methyl pentanoate	81.72159	81.726	0.00005
$C_7H_{14}O_2$	Methyl hexanoate	93.87929	93.891	0.00012
$C_8H_{16}O_2$	Methyl heptanoate	106.03699	106.079	0.00040
$C_9H_{18}O_2$	Methyl octanoate	118.19469	118.217	0.00018
$C_{10}H_{20}O_2$	Methyl nonanoate	130.35239	130.373	0.00016
$C_{11}H_{22}O_2$	Methyl decanoate	142.51009	142.523	0.00009
$C_{12}H_{24}O_2$	Methyl undecanoate	154.66779	154.677	0.00006
$C_{13}H_{26}O_2$	Methyl dodecanoate	166.82549	166.842	0.00010
$C_{14}H_{28}O_2$	Methyl tridecanoate	178.98319	179.000	0.00009
$C_{15}H_{30}O_2$	Methyl tetradecanoate	191.14089	191.170	0.00015
$C_{16}H_{32}O_2$	Methyl pentadecanoate	203.29859	203.356	0.00028
$C_4H_8O_2$	Propyl formate	57.76366	57.746	-0.00030
$C_4H_8O_2$	Ethyl acetate	57.63888	57.548	-0.00157
$C_5H_{10}O_2$	Isopropyl acetate	69.89747	69.889	-0.00013
$C_5H_{10}O_2$	Ethyl propanoate	69.79658	69.700	-0.00139
$C_6H_{12}O_2$	Butyl acetate	81.95428	81.873	-0.00099
$C_6H_{12}O_2$	t-Butyl acetate	82.23881	82.197	-0.00051

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_{12}O_2$	Methyl 2,2-dimethylpropanoate	82.00612	81.935	-0.00087
$C_7H_{14}O_2$	Ethyl pentanoate	94.11198	94.033	-0.00084
$C_7H_{14}O_2$	Ethyl 3-methylbutanoate	94.18454	94.252	0.00072
$C_7H_{14}O_2$	Ethyl 2,2-dimethylpropanoate	94.39651	94.345	-0.00054
$C_8H_{16}O_2$	Isobutyl isobutanoate	106.44313	106.363	-0.00075
$C_8H_{16}O_2$	Propyl pentanoate	106.26968	106.267	-0.00003
$C_8H_{16}O_2$	Isopropyl pentanoate	106.37057	106.384	0.00013
$C_9H_{18}O_2$	Butyl pentanoate	118.42738	118.489	0.00052
$C_9H_{18}O_2$	sec-Butyl pentanoate	118.52827	118.624	0.00081
$C_9H_{18}O_2$	Isobutyl pentanoate	118.49994	118.576	0.00064

Table 1.19. The calculated and experimental total bond energies of amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO	Formamide	23.68712	23.697	0.00041
C_2H_5NO	Acetamide	36.15222	36.103	-0.00135
C_3H_7NO	Propanamide	48.30992	48.264	-0.00094
C_4H_9NO	Butanamide	60.46762	60.449	-0.00030
C_4H_9NO	2-Methylpropanamide	60.51509	60.455	-0.00099
$C_5H_{11}NO$	Pentanamide	72.62532	72.481	-0.00200
$C_5H_{11}NO$	2,2-Dimethylpropanamide	72.67890	72.718	0.00054
$C_6H_{13}NO$	Hexanamide	84.78302	84.780	-0.00004
$C_8H_{17}NO$	Octanamide	109.09842	109.071	-0.00025

Table 1.20. The calculated and experimental total bond energies of N-alkyl and N,N-dialkyl amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_7NO	N,N-Dimethylformamide	47.53142	47.574	0.00090
C_4H_9NO	N,N-Dimethylacetamide	59.91404	59.890	-0.00041
$C_6H_{13}NO$	N-Butylacetamide	84.63649	84.590	-0.00055

Table 1.21. The calculated and experimental total bond energies of urea using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4N_2O	Urea	31.35919	31.393	0.00108

Table 1.22. The calculated and experimental total bond energies of acid halide using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3ClO	Acetyl chloride	28.02174	27.990	-0.00115

Table 1.23. The calculated and experimental total bond energies of acid anhydrides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_6O_3$	Acetic anhydride	56.94096	56.948	0.00013
$C_6H_{10}O_3$	Propanoic anhydride	81.25636	81.401	0.00177

Table 1.24. The calculated and experimental total bond energies of nitriles using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3N	Acetonitrile	25.72060	25.77	0.00174
C_3H_5N	Propanenitrile	37.87830	37.94	0.00171
C_4H_7N	Butanenitrile	50.03600	50.08	0.00082
C_4H_7N	2-Methylpropanenitrile	50.13689	50.18	0.00092
C_5H_9N	Pentanenitrile	62.19370	62.26	0.00111
C_5H_9N	2,2-Dimethylpropanenitrile	62.47823	62.40	-0.00132
$C_7H_{13}N$	Heptanenitrile	86.50910	86.59	0.00089
$C_8H_{15}N$	Octanenitrile	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	171.61300	171.70	0.00052

Table 1.25. The calculated and experimental total bond energies of thiols using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
HS	Hydrogen Sulfide	3.77430	3.653	-0.03320
H_2S	Dihydrogen Sulfide	7.56058	7.605	0.00582
CH_4S	Methanethiol	19.60264	19.575	-0.00141
C_2H_6S	Ethanethiol	31.76034	31.762	0.00005
C_3H_8S	1-Propanethiol	43.91804	43.933	0.00035
C_3H_8S	2-Propanethiol	44.01893	44.020	0.00003
$C_4H_{10}S$	1-Butanethiol	56.07574	56.089	0.00024
$C_4H_{10}S$	2-Butanethiol	56.17663	56.181	0.00009
$C_4H_{10}S$	2-Methyl-1-propanethiol	56.14830	56.186	0.00066
$C_4H_{10}S$	2-Methyl-2-propanethiol	56.36027	56.313	-0.00084
$C_5H_{12}S$	2-Methyl-1-butanethiol	68.30600	68.314	0.00012
$C_5H_{12}S$	1-Pentanethiol	68.23344	68.264	0.00044
$C_5H_{12}S$	2-Methyl-2-butanethiol	68.51797	68.441	-0.00113
$C_5H_{12}S$	3-Methyl-2-butanethiol	68.31552	68.381	0.00095
$C_5H_{12}S$	2,2-Dimethyl-1-propanethiol	68.51797	68.461	-0.00084
$C_6H_{14}S$	1-Hexanethiol	80.39114	80.416	0.00031
$C_6H_{14}S$	2-Methyl-2-pentanethiol	80.67567	80.607	-0.00085
$C_6H_{14}S$	2,3-Dimethyl-2-butanethiol	80.71992	80.603	-0.00145
$C_7H_{16}S$	1-Heptanethiol	92.54884	92.570	0.00023
$C_{10}H_{22}S$	1-Decanethiol	129.02194	129.048	0.00020

Table 1.26. The calculated and experimental total bond energies of sulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6S	Dimethyl sulfide	31.65668	31.672	0.00048
C_3H_8S	Ethyl methyl sulfide	43.81438	43.848	0.00078
$C_4H_{10}S$	Diethyl sulfide	55.97208	56.043	0.00126
$C_4H_{10}S$	Methyl propyl sulfide	55.97208	56.029	0.00102
$C_4H_{10}S$	Isopropyl methyl sulfide	56.07297	56.115	0.00075
$C_5H_{12}S$	Butyl methyl sulfide	68.12978	68.185	0.00081
$C_5H_{12}S$	t-Butyl methyl sulfide	68.28245	68.381	0.00144
$C_5H_{12}S$	Ethyl propyl sulfide	68.12978	68.210	0.00117
$C_5H_{12}S$	Ethyl isopropyl sulfide	68.23067	68.350	0.00174
$C_6H_{14}S$	Diisopropyl sulfide	80.48926	80.542	0.00065
$C_6H_{14}S$	Butyl ethyl sulfide	80.28748	80.395	0.00133
$C_6H_{14}S$	Methyl pentyl sulfide	80.28748	80.332	0.00056
$C_8H_{18}S$	Dibutyl sulfide	104.60288	104.701	0.00094
$C_8H_{18}S$	Di-sec-butyl sulfide	104.80466	104.701	-0.00099
$C_8H_{18}S$	Di-t-butyl sulfide	104.90822	104.920	0.00011
$C_8H_{18}S$	Diisobutyl sulfide	104.74800	104.834	0.00082
$C_{10}H_{22}S$	Ethyl propyl sulfide	128.91828	128.979	0.00047
$C_{10}H_{22}S$	Diisopentyl sulfide	129.06340	129.151	0.00068

Table 1.27. The calculated and experimental total bond energies of disulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6S_2$	Dimethyl disulfide	34.48127	34.413	-0.00199
$C_4H_{10}S_2$	Diethyl disulfide	58.79667	58.873	0.00129
$C_6H_{14}S_2$	Dipropyl disulfide	83.11207	83.169	0.00068
$C_8H_{18}S_2$	Di-t-butyl disulfide	107.99653	107.919	-0.00072

Table 1.28. The calculated and experimental total bond energies of sulfoxides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6SO	Dimethyl sulfoxide	35.52450	35.435	-0.00253
$C_4H_{10}SO$	Diethyl sulfoxide	59.83990	59.891	0.00085
$C_6H_{14}SO$	Dipropyl sulfoxide	84.15530	84.294	0.00165

Table 1.29. The calculated and experimental total bond energies of sulfones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_2$	Dimethyl sulfone	40.27588	40.316	0.00100

Table 1.30. The calculated and experimental total bond energies of sulfites using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_3$	Dimethyl sulfite	43.95058	44.042	0.00207
$C_4H_{10}SO_3$	Diethyl sulfite	68.54939	68.648	0.00143
$C_8H_{18}SO_3$	Dibutyl sulfite	117.18019	117.191	0.00009

Table 1.31. The calculated and experimental total bond energies of sulfates using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_4$	Dimethyl sulfate	48.70617	48.734	0.00058
$C_4H_{10}SO_4$	Diethyl sulfate	73.30077	73.346	0.00061
$C_6H_{14}SO_4$	Dipropyl sulfate	97.61617	97.609	-0.00008

Table 1.32. The calculated and experimental total bond energies of nitro alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Nitromethane	25.14934	25.107	-0.00168
$C_2H_5NO_2$	Nitroethane	37.30704	37.292	-0.00040
$C_3H_7NO_2$	1-Nitropropane	49.46474	49.451	-0.00028
$C_3H_7NO_2$	2-Nitropropane	49.56563	49.602	0.00074
$C_4H_9NO_2$	1-Nitrobutane	61.62244	61.601	-0.00036
$C_4H_9NO_2$	2-Nitroisobutane	61.90697	61.945	0.00061
$C_5H_{11}NO_2$	1-Nitropentane	73.78014	73.759	-0.00028

Table 1.33. The calculated and experimental total bond energies of nitrite using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Methyl nitrite	24.92328	24.955	0.00126

Table 1.34. The calculated and experimental total bond energies of nitrate using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_3	Methyl nitrate	28.18536	28.117	-0.00244
$C_2H_5NO_3$	Ethyl nitrate	40.34306	40.396	0.00131
$C_3H_7NO_3$	Propyl nitrate	52.50076	52.550	0.00093
$C_3H_7NO_3$	Isopropyl nitrate	52.60165	52.725	0.00233

Table 1.35. The calculated and experimental total bond energies of conjugated alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_5H_8	Cyclopentene	54.83565	54.86117	0.00047
C_4H_6	1,3 Butadiene	42.09159	42.12705	0.00084
C_5H_8	1,3 Pentadiene	54.40776	54.42484	0.00031
C_5H_8	1,4 Pentadiene	54.03745	54.11806	0.00149
C_5H_6	1,3 Cyclopentadiene	49.27432	49.30294	0.00058

Table 1.36. The calculated and experimental total bond energies of aromatics and heterocyclic aromatics using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6	Benzene	57.26008	57.26340	0.00006
C_6H_5Cl	Chlorobenzene	56.55263	56.581	0.00051
$C_6H_4Cl_2$	m-dichlorobenzene	55.84518	55.852	0.00012
$C_6H_3Cl_3$	1,2,3-trichlorobenzene	55.13773	55.077	-0.00111
$C_6H_3Cl_3$	1,3,5-trichlorbenzene	55.29542	55.255	-0.00073
C_6Cl_6	Hexachlorobenzene	52.57130	52.477	-0.00179
$C_6H_5NO_2$	Nitrobenzene	65.18754	65.217	0.00046
C_7H_8	Toluene	69.48425	69.546	0.00088
$C_7H_6O_2$	Benzoic acid	73.76938	73.762	-0.00009
$C_7H_5ClO_2$	2-chlorobenzoic acid	73.06193	73.082	0.00027
$C_7H_5ClO_2$	3-chlorobenzoic acid	73.26820	73.261	-0.00010
$C_7H_5ClO_2$	4-chlorobenzoic acid	73.26820	73.247	-0.00028
C_6H_7N	Aniline	64.43373	64.374	-0.00093
C_7H_9N	2-methylaniline	76.62345	76.643	-0.00025
C_7H_9N	3-methylaniline	76.62345	76.661	0.00050
C_7H_9N	4-methylaniline	76.62345	76.654	0.00040
$C_6H_6N_2O_2$	2-nitroaniline	72.47476	72.424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	72.47476	72.476	-0.00002
$C_7H_7NO_2$	Aniline-2-carboxylic acid	80.90857	80.941	0.00041
$C_7H_7NO_2$	Aniline-3-carboxylic acid	80.90857	80.813	-0.00118
$C_7H_7NO_2$	Aniline-4-carboxylic acid	80.90857	80.949	0.00050
C_6H_6O	Phenol	61.75817	61.704	-0.00087
$C_6H_4N_2O_5$	2,4-dinitrophenol	77.61308	77.642	0.00037
C_6H_8O	Anisole	73.39006	73.355	-0.00047
$C_{10}H_8$	Naphthalene	90.74658	90.79143	0.00049
C_4H_5N	Pyrrole	44.81090	44.785	-0.00057
C_4H_4O	Furan	41.67782	41.692	0.00033
C_4H_4S	Thiophene	40.42501	40.430	0.00013
$C_3H_4N_2$	Imidazole	39.76343	39.74106	-0.00056
C_5H_5N	Pyridine	51.91802	51.87927	-0.00075
$C_4H_4N_2$	Pyrimidine	46.57597	46.51794	-0.00125
$C_4H_4N_2$	Pyrazine	46.57597	46.51380	0.00095
C_9H_7N	Quinoline	85.40453	85.48607	0.00178
C_9H_7N	Isoquinoline	85.40453	85.44358	0.00046
C_8H_7N	Indole	78.52215	78.514	-0.00010
$C_5H_5N_5$	Adenine	70.83735	70.79811	-0.00055

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Section V1

Software Program

The present invention relates to a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising: processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

In one embodiment, for example, the system comprises five components: (1) the graphical user interface (GUI); (2) the routine for parsing between an input chemical structure or name and taking the input and activating a routine to call up the parts of the molecule (functional groups), which are used for determining the energies and structure to be rendered; (3) the functional-group data base that has an organization of the theoretical solutions; (4) the rendering engine, which calculates and enables manipulations of the image, such as a three-dimensional model in response to commands, as well as responds to commands for data parameters corresponding to the image such as bond energies and charge distribution and geometrical parameters; and (5) data transfer system for inputting numerical data into or out of the computational components and storage components of the main system. The system further comprises spreadsheets with solutions of the bond parameters with output in any standard spreadsheet format. The system also comprises a data-handling program to transfer data from the spreadsheets into the main program.

The output may be, for example, at least one of graphical, simulation, text, and numerical data. The output may be the calculation of at least one of: (1) a bond distance between two atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

In other embodiments, the charge, current, energy, and geometrical parameters are output to be inputs to other programs that may be used in further applications. For example, the data of heats of formation may be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways. That is, a novel composition of matter may be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The charge and current density functions may be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species. These fields and the predictions of field interactions may be computed using Maxwell's equations. In one embodiment, finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index. Furthermore, the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization. Furthermore, the data can be input into other programs of the system, which calculate thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

The output data may be used to predict a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The novel property, for example, may be a new pharmaceutical use, or stability at room temperature of a novel arrangement of atoms or ions.

In one embodiment, the output device of the system is a display that displays at least one of visual or graphical media. The display may be at least one of static or dynamic. At least one of vibration, rotation, and translation may be displayed. The displayed information

may be used for at least one of modeling reactivity, predicting physical properties, and aiding in drug and material design. The output device may be a monitor, video projector, printer, or one-, two- or three-dimensional rendering device. The displayed information may be used to model other molecules and provides utility to anticipate their reactivity and physical properties. Additionally, data may be output and used in the same and additional applications as the rendered models and representations of the calculated physical solutions. The processing means of the system may be a general-purpose computer. The general-purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input means. The input means may comprise a serial port, USB port, microphone input, camera input, keyboard or mouse. The processing means comprises a special purpose computer or other hardware system. The system may comprise computer program products such as computer readable medium having embodied therein program code means. The computer readable media may be any available media which can be accessed by a general purpose or special purpose computer. The computer readable media may comprise, for example, at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium that can embody the desired program code means and which can be accessed by a general purpose or special purpose computer. The program code means may comprise executable instructions and data, which cause a general purpose computer or special purpose computer to perform a certain function of a group of functions. Commercial examples of suitable program language includes, for example, C++, C, JAVA, FORTRAN, Python and Assembly Languages, programmed with an algorithm based on the physical solutions, and the computer may be a PC, mainframe, supercomputer, or cluster of computers. Commercial examples of suitable programs include, for example, APIs like OpenGL, DirectX, FOX GUI toolkit, and Qt. This program may be developed to run on at least one of operating systems like Windows XP, Windows 2000, Windows Vista, MAC OS, MAC OS X, Linux, Unix, Irix and other Unix-type operating systems.

Millsian software is designed to render 3-D models of molecules, molecular ions, molecular radicals, functional groups thereof, and related structure and property information and produce useful data output and application of the parameters of these species, wherein the nature of their bound electrons and chemical bonds are solved using Dr. Randell L. Mills' Classical Quantum Mechanics theory described in the reference: R. L. Mills, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional

Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at http://www.blacklightpower.com/bookdownload.shtml, which is incorporated by this reference in its entirety. Figure 76 provides a flow chart diagram, which is an example of a software system that can be utilized for this purpose, which example is not intended to limit the scope of the disclosed inventions. The main parts of this exemplary software system illustrated in Figure 76 will now be further explained:

Start: A user can start the program by running an executable program file. That might be done, for example, by double clicking the program icon on a Windows-based operating system, or typing the name of the executable file on the command line and pressing the 'Enter' key on a Linux or Unix operating system. The program initially starts by reading data files located in specific directories. The names of those directories and locations are fixed according to the type and format of the data files.

Data files: There are two types of data files used in the software system: functional group data files and molecule data files. Functional group data files contain information about various functional groups. Functional groups are the basic bonding elements or units that each typically comprise an atom, or at least two atoms bound together as found within a molecule (e.g. -Cl , C=C, C=O, CH3). Functional groups typically dictate or define properties and structure of the molecule. Similar functional groups in different molecules typically react in similar ways when subjected to a particular set of reaction conditions. Molecule data files contain information about molecules, molecular ions, and molecular radicals. These data files are processed according to their file formats.

File formats: Millsian software employs two kinds of file formats for storing information about the structure, energies and names of molecules and functional groups: raw-data format and hierarchical format. In a raw-data file, all information is stored as is, below the header describing the type of information. As shown in the Table below, for example, the names of the molecule or functional group are listed below the #NAMES header. The names and positions of the atoms are listed below the #ATOMS header, and so on.

```
#NAMES
CH3
Alkane CH3

#SMILES
C-

#ATOMS
1       C       0       0       0
2       H       1.9775 -0.698 0
3       H       -0.9888         -0.698  1.712
4       H       -0.9888         -0.698  -1.712

#AO
1       1 1s    0.171   2
2       1 2sp3  0.864   -1

#BONDS
1       1 2     1       1.649
2       1 3     1       1.649
3       1 4     1       1.649

#BONDAXES
1       1       1       90      0       0

#DATA
RCH bond angle: 109.44°
CH bond length: 2.097 a
HFORM: 12.492
```

Most of the functional groups files and some simple molecule files are stored in raw data format. The other file format used with the Millsian software system, the hierarchical file format, represents the information in a graph style, in which nodes are connected to other nodes through links. This format is designed to construct molecules by attaching different functional groups in a desired manner. Using this file format, the user can construct complex molecules built from solved functional groups.

For example, as shown in the Table below, the pentane data file includes a #GROUPS header below which is list all of the functional groups that form a part of the pentane molecule. Under the #GROUP_LINKS header is information about how these functional groups are connected to each other to construct pentane.

```
#NAMES
Pentane

#SMILES
CCCCC

#GROUPS
1       C-
2       -C-
3       -C-
4       -C-
5       C-


#GROUP_LINKS
1       1 1     2 1     180
2       2 2     3 1     180
3       3 2     4 1     180
4       4 2     5 1     180
```

Processing data files: As further shown in the flow diagram of Figure 76 for the exemplary Millsian software system, the program first processes the functional group data file and constructs the functional-group objects, which are complete 3-D representations of the functional groups and their related information supplied in the corresponding file. These objects are then ready to be visually displayed through use of a molecule viewer. Next, the program processes the molecule data file. If the molecule date file is in raw-data format, then the program makes a molecule object directly from it. If the file is in hierarchical format, then the program calculates geometric parameters from listed functional groups. The program stores all functional-group objects and molecule objects using internal data structures.

Visualization/ User Interactions: As shown in Figures 77 and 78, the molecule viewer displays the functional-group objects and molecule objects and provides basic interaction capabilities with the displayed objects, such as rotating, scaling, and moving the objects. The molecule viewer also provides other visualization options, such as viewing molecules in wire frame mode, viewing coordinate axes, and changing of the transparency and lighting. The user, for example, can also select parts of a molecule for visualization, like a nucleus, atomic orbital, molecular orbital, or bond axis. The viewer also includes a drop down information window, which provides, for example, related information about molecules, such as bond angles, component functional groups, and total heat of formation. In one embodiment, a user can create new molecules by joining functional groups. For this purpose, the user can select a

first functional group. Next, the user can select an open bond from the functional group where the user desires to attach another group. Next, the user can select another or the same functional group, followed by selecting an open bond from the other group. The user can join the two selected functional groups at the selected open bonds by clicking on 'Join Groups'. This method of joining functional groups at open bonds can be repeated to form the desired molecule.

SMILES input: The Simplified Molecular Input Line Entry Specification or SMILES is a specification for unambiguously describing the structure of chemical molecules using short ASCII strings. Through the user interface, a user can enter SMILES to construct molecules, provided the new molecule comprises functional groups that are in the database. Once a SMILES is entered, a parser reads in and breaks it down into component functional groups. The software system then attaches the component functional groups to create the new molecule object, which can then be viewed using the molecule viewer.

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

CONTINUOUS-CHAIN ALKANES (C_nH_{2n+2}, $n=3,4,5...\infty$)

The continuous-chain alkanes, C_nH_{2n+2}, are the homologous series comprising terminal methyl groups at each end of the chain with $n-2$ methylene (CH_2) groups in between:

$$CH_3\left(CH_2\right)_{n-2}CH_3 \tag{15.109}$$

C_nH_{2n+2} can be solved using the same principles as those used to solve ethane and ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three H AOs combine with three carbon $2sp^3$ HOs and two H AOs combine with two carbon $2sp^3$ HOs to form each methyl and methylene group, respectively, where each bond comprises a H_2-type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The CH_3 and CH_2 groups bond by forming H_2-type MOs between the remaining $C2sp^3$ HOs on the carbons such that each carbon forms four bonds involving its four $C2sp^3$ HOs. For the alkyl $C-C$ group, $E_T\left(atom-atom,msp^3.AO\right)$ is $-1.85836\,eV$ where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the chain comprising methylene groups and terminal methyl groups.

The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of straight-chain alkanes are given in Tables 15.4, 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.8. In this angle table and those given in subsequent sections when c_2' is given as the ratio of two values of c_2 designated to Atom 1 and Atom 2 and corresponding to $E_{Coulombic}$ of Atom 1 and Atom 2, respectively, then $c_2'=\dfrac{c_2\left(Atom\ 2\right)}{c_2\left(Atom\ 1\right)}$.

Table 15.4. The geometrical bond parameters of straight-chain alkanes and experimental values [1].

Parameter	$C-C$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group
$a\ (a_0)$	2.12499	1.64920	1.67122
$c'\ (a_0)$	1.45744	1.04856	1.05553
Bond Length $2c'\ (A)$	1.54280	1.10974	1.11713
Exp. Bond Length (A)	1.532 (propane) 1.531 (butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)
$b,c\ (a_0)$	1.54616	1.27295	1.29569
e	0.68600	0.63580	0.63159

Table 15.5. The MO to HO intercept geometrical bond parameters of straight-chain alkanes. E_T is $E_T(atom-atom, nsp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Unshared}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$H_3C_a-C_bH_2CH_2$	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_a-C_bH_2CH_2$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117

Table 15.6. The energy parameters (eV) of functional groups of straight-chain alkanes.

Parameters	$C-C$ Group	CH_3 Group	CH_2 Group
n_1	1	3	2
n_2	0	2	1
n_3	0	0	0
C_1	0.5	0.75	0.75
C_2	1	1	1
c_1	1	1	1
c_2	0.91771	0.91771	0.91771
c_3	0	0	1
c_4	2	1	1
c_5	0	3	2
C_{1o}	0.5	0.75	0.75
C_{2o}	1	1	1
$V_e\ (eV)$	-28.79214	-107.32728	-70.41425
$V_p\ (eV)$	9.33352	38.92728	25.78002
$T\ (eV)$	6.77464	32.53914	21.06675
$V_m\ (eV)$	-3.38732	-16.26957	-10.53337
$E_{(AO/HO)}\ (eV)$	-15.56407	-15.56407	-15.56407
$\Delta E_{H_2MO(AO/HO)}\ (eV)$	0	0	0
$E_{T(AO/HO)}\ (eV)$	-15.56407	-15.56407	-15.56407
$E_{T(H_2MO)}\ (eV)$	-31.63537	-67.69451	-49.66493
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-1.85836	0	0
$E_{T(MO)}\ (eV)$	-33.49373	-67.69450	-49.66493
$\omega\ \left(10^{15}\ rad/s\right)$	9.43699	24.9286	24.2751
$E_K\ (eV)$	6.21159	16.40846	15.97831
$\overline{E}_D\ (eV)$	-0.16515	-0.25352	-0.25017
$\overline{E}_{Kvib}\ (eV)$	0.12312 [2]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))
$\overline{E}_{osc}\ (eV)$	-0.10359	-0.22757	-0.14502
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803
$E_{T(Group)}\ (eV)$	-33.59732	-67.92207	-49.80996
$E_{initial(c_4\ AO/HO)}\ (eV)$	-14.63489	-14.63489	-14.63489
$E_{initial(c_5\ AO/HO)}\ (eV)$	0	-13.59844	-13.59844
$E_{D(Group)}\ (eV)$	4.32754	12.49186	7.83016

Table 15.7. The total bond energies of n-alkanes calculated using the functional group composition and the energies of Table 15.6 compared to the experimental values [3].

Formula	Name	$C-C$	CH_3	CH_2	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_8	Propane	2	2	1	41.46896	41.434	-0.00085
C_4H_{10}	Butane	3	2	2	53.62666	53.61	-0.00036
C_5H_{12}	Pentane	4	2	3	65.78436	65.77	-0.00017
C_6H_{14}	Hexane	5	2	4	77.94206	77.93	-0.00019
C_7H_{16}	Heptane	6	2	5	90.09976	90.09	-0.00013
C_8H_{18}	Octane	7	2	6	102.25746	102.25	-0.00006
C_9H_{20}	Nonane	8	2	7	114.41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	9	2	8	126.57286	126.57	-0.00003
$C_{11}H_{24}$	Undecane	10	2	9	138.73056	138.736	0.00004
$C_{12}H_{26}$	Dodecane	11	2	10	150.88826	150.88	-0.00008
$C_{18}H_{38}$	Octadecane	18	2	16	223.83446	223.85	0.00008

Table 15.8. The bond angle parameters of straight-chain alkanes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493 C_a	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493 C_a	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	

BRANCHED ALKANES (C_nH_{2n+2}, $n=3,4,5...\infty$)

The branched-chain alkanes, C_nH_{2n+2}, comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those used to solve the methyl and methylene functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is $-1.85836\,eV$ or $-1.44915\,eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\,eV$ (Eq. (14.513), or methyl, $-0.72457\,eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.12 corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.14.

Table 15.9. The symbols of functional groups of branched alkanes.

Functional Group	Group Symbol
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.10. The geometrical bond parameters of branched alkanes and experimental values [1].

Parameter	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,e\ (a_0)$	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.11. The MO to HO intercept geometrical bond parameters of branched-chain alkanes. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Coulomb}(C'2sp^3)$ (eV) Final	$E(C'2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\ (a_0)$	$d_2\ (a_0)$
$C-H\ (CH_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC_bH_2CH_2-$ ($C'-C$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC'_bH_2CH_2-$ ($C'-C$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC'_b\left(H_2C_c-R'\right)HCH_2-$ ($C'-C$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C'_b\left(R''-H_2C_c\right)CH_2-$ ($C'-C$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_a\left(H_2C_c-R'\right)HCH_2-$ ($C'-C$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a\left(R'-H_2C_d\right)C'_b\left(R''-H_2C_c\right)CH_2-$ ($C'-C$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_a\left(H_2C_c-R'\right)HCH_2-$ ($C'-C$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C'-C$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.12. The energy parameters (eV) of functional groups of branched-chain alkanes.

Parameters	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	3	2	1	1	1	1	1	1	1
n_2	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0
C_1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	1	1	0	0	0	1	1	0
c_4	1	1	1	2	2	2	2	2	2
c_5	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1
V_r (eV)	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO/MO)$ (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO/MO)$ (eV)	0	0	0	0	0	0	0	0	0
$E_T(AO/MO)$ (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{asc}$ (eV)	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{magc} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(group)$ (eV)	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_1.AO/MO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_2.AO/MO)$ (eV)	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(group)$ (eV)	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.13. The total bond energies of branched alkanes calculated using the functional group composition and the energies of Table 15.12 compared to the experimental values [3].

Formula	Name	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_{10}	Isobutane	3	0	1	0	3	0	0	0	0	53.69922	53.695	-0.00007
C_5H_{12}	Isopentane	3	1	1	1	3	0	0	0	0	65.85692	65.843	-0.00021
C_5H_{12}	Neopentane	4	0	0	0	0	4	0	0	0	65.86336	65.992	0.00195
C_6H_{14}	2-Methylpentane	3	2	1	2	3	0	0	0	0	78.01462	78.007	-0.00010
C_6H_{14}	3-Methylpentane	3	2	1	2	3	0	0	0	0	78.01462	77.979	-0.00046
C_6H_{14}	2,2-Dimethylbutane	4	1	0	1	0	4	0	0	0	78.02106	78.124	0.00132
C_6H_{14}	2,3-Dimethylbutane	4	0	2	0	4	0	1	0	0	77.99581	78.043	0.00061
C_7H_{16}	2-Methylhexane	3	3	1	3	3	0	0	0	0	90.17232	90.160	-0.00014
C_7H_{16}	3-Methylhexane	3	3	1	3	3	0	0	0	0	90.17232	90.127	-0.00051
C_7H_{16}	3-Ethylpentane	3	3	1	3	3	0	0	0	0	90.17232	90.108	-0.00072
C_7H_{16}	2,2-Dimethylpentane	4	2	0	2	0	4	0	0	0	90.17876	90.276	0.00107
C_7H_{16}	2,2,3-Trimethylbutane	5	0	1	0	2	3	0	0	1	90.22301	90.262	0.00044
C_7H_{16}	2,4-Dimethylpentane	4	1	2	0	6	0	0	0	0	90.24488	90.233	-0.00013
C_7H_{16}	3,3-Dimethylpentane	4	2	0	2	0	4	0	0	0	90.17876	90.227	0.00054
C_8H_{18}	2-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.322	-0.00008
C_8H_{18}	3-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.293	-0.00036
C_8H_{18}	4-Methylheptane	3	4	1	4	3	0	0	0	0	102.33002	102.286	-0.00043
C_8H_{18}	3-Ethylhexane	3	4	1	3	4	0	0	0	0	102.30169	102.274	-0.00027
C_8H_{18}	2,2-Dimethylhexane	4	3	0	3	0	4	0	0	0	102.33646	102.417	0.00079
C_8H_{18}	2,3-Dimethylhexane	4	2	2	2	4	0	1	0	0	102.31121	102.306	-0.00005
C_8H_{18}	2,4-Dimethylhexane	4	2	2	1	6	0	0	0	0	102.40258	102.362	-0.00040
C_8H_{18}	2,5-Dimethylhexane	4	2	2	1	6	0	0	0	0	102.40258	102.396	-0.00006
C_8H_{18}	3,3-Dimethylhexane	4	3	0	3	0	4	0	0	0	102.33646	102.369	0.00032
C_8H_{18}	3,4-Dimethylhexane	4	2	2	2	4	0	1	0	0	102.31121	102.296	-0.00015
C_8H_{18}	3-Ethyl-2-methylpentane	4	2	2	2	4	0	1	0	0	102.31121	102.277	-0.00033
C_8H_{18}	3-Ethyl-3-methylpentane	4	3	0	3	0	4	0	0	0	102.33646	102.317	-0.00019
C_8H_{18}	2,2,3-Trimethylpentane	5	1	1	1	2	3	0	0	1	102.38071	102.370	-0.00010
C_8H_{18}	2,2,4-Trimethylpentane	5	1	1	0	3	4	0	0	0	102.40902	102.412	0.00003
C_8H_{18}	2,3,3-Trimethylpentane	5	1	1	1	2	3	0	0	1	102.38071	102.332	-0.00048
C_8H_{18}	2,3,4-Trimethylpentane	5	0	3	0	5	0	2	0	0	102.29240	102.342	0.00049
C_8H_{18}	2,2,3,3-Tetramethylbutane	6	0	0	0	0	6	0	1	0	102.41632	102.433	0.00016
C_9H_{20}	2,3,5-Trimethylhexane	5	1	3	0	7	0	1	0	0	114.54147	114.551	0.00008
C_9H_{20}	3,3-Diethylpentane	4	4	0	4	0	4	0	0	0	114.49416	114.455	-0.00034
C_9H_{20}	2,2,3,3-Tetramethylpentane	6	1	0	1	0	6	0	1	0	114.57402	114.494	-0.00070
C_9H_{20}	2,2,3,4-Tetramethylpentane	6	0	2	0	3	3	1	0	1	114.51960	114.492	-0.00024
C_9H_{20}	2,2,4,4-Tetramethylpentane	6	1	0	0	0	8	0	0	0	114.57316	114.541	-0.00028
C_9H_{20}	2,3,3,4-Tetramethylpentane	6	0	2	0	4	2	0	0	2	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	3	6	1	6	3	0	0	0	0	126.64542	126.680	0.00027
$C_{10}H_{22}$	5-Methylnonane	3	6	1	6	3	0	0	0	0	126.64542	126.663	0.00014

Table 15.14. The bond angle parameters of branched-chain alkanes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKENES (C_nH_{2n}, $n=3,4,5...\infty$)

The straight and branched-chain alkenes, C_nH_{2n}, comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified: C vinyl single bond to $-C(C)=C$, C vinyl single bond to $-C(H)=C$, and C vinyl single bond to $-C(C)=CH_2$. In addition, CH_2 of the $-C=CH_2$ moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759\,eV$, given by Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.52) is $-1.85836\,eV$ or $-1.44915\,eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\,eV$ (Eq. (14.513), or methyl, $-0.72457\,eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.71-15.78)), and energy (Eqs.

(15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkenes determined using Eqs. (15.79-15.108) are given in Table 15.20.

Table J.5.15. The symbols of functional groups of alkenes.

Functional Group	Group Symbol
CC double bond	$C=C$
C vinyl single bond to -C(C)=C	$C-C$ (i)
C vinyl single bond to -C(H)=C	$C-C$ (ii)
C vinyl single *bond to* -C(C)=CH$_2$	$C-C$ (iii)
CH$_2$ alkenyl group	$C-H\ (CH_2)$ (i)
CH$_2$ group	$C-H\ (CH_2)$
CH$_2$ alkyl group	$C-H\ (CH_2)$ (ii)
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.16. The geometrical bond parameters of alkenes and experimental values [1].

Parameter	$C=C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-C$ (iii) Group	$C-H\ (CH_2)$ (i) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ (ii) Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.47228	2.04740	2.04740	2.04740	1.64010	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.26661	1.43087	1.43087	1.43087	1.04566	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (A)$	1.34052	1.51437	1.51437	1.51437	1.10668	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.342 (2-methylpropene) 1.346 (2-butene) 1.349 (1,3-butadiene)		1.508 (2-butene)	1.508 (2-methylpropene)	1.10 (2-methylpropene) 1.108 (avg.) (1,3-butadiene)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.75055	1.46439	1.46439	1.46439	1.26354	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
c	0.86030	0.69887	0.69887	0.69887	0.63756	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.17. The MO to HO intercept geometrical bond parameters of alkenes. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ $\left(a_0\right)$	r_{final} $\left(a_0\right)$	$E_{Coulomb}\left(C2sp^3\right)$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 $\left(a_0\right)$	d_2 $\left(a_0\right)$
$C_c\left(H\right)C_{sp}=C_{sp}\left(H\right)C_{sd}$	C_{sp}	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0.49168
$C_c\left(H\right)C_{sp}=C_bH_2$	C_b	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	129.84	50.16	60.70	0.72040	0.54620
$C_c\left(C_{sd}\right)C_{sp}=C_bH,C_c$	C_{sp}	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	126.39	53.61	56.95	0.80289	0.46371
$R_1C_bH_2-C_{sp}(C)=C$ (C−C (i))	C_{sp}	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	60.88	119.12	27.79	1.81127	0.38039
$R_1C_bH_2-C_{sp}(C)=C$ (C−C (i)) $R_1C_bH_2-C_{sp}(C)=CH_2$ (C−C (iii))	C_b	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	67.40	112.60	31.36	1.74821	0.31734
$R_1C_bH_2-C_{sp}(H)=C$ (C−C (ii))	C_{sp}	-1.13380	-0.92918	0	0	-153.67866	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$R_1C_bH_2-C_{sp}(H)=C$ (C−C (i))	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C-H\left(CH_2\right)$ (i)	C	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	77.15	102.85	41.13	1.23531	0.18965
$C-H\left(CH_3\right)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_2\right)$ (ii)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\left(CH\right)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_{sp}C_bH_2CH_2-$ (C−C (a))	C_{sp}	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_{sp}C_bH_2CH_2-$ (C−C (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_{sp}C_b\left(H_2C_c-R'\right)HCH_2-$ (C−C (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_{sp}\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ (C−C (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_{sp}C_b\left(H_2C_c-R'\right)HCH_2-$ (C−C (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_{sp}\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ (C−C (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_{sp}C_b\left(H_2C_c-R'\right)HCH_2-$ (C−C (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_{sp}\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ (C−C (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.18. The energy parameters (eV) of functional groups of alkenes.

Parameters	$C=C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-C$ (iii) Group	CH_2 (i) Group	CH_3 Group	CH_2 (ii) Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	1	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	1	0	1	1	0	1	1	0	0	0	1	1	0
c_4	4	2	2	2	1	1	1	1	2	2	2	2	2	2
c_5	0	0	0	0	2	3	2	1	0	0	0	0	0	0
$C_{1\sigma}$	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{2\sigma}$	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-102.08992	-30.19634	-30.19634	-30.19634	-72.03287	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	21.48386	9.50874	9.50874	9.50874	26.02344	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	34.67062	7.37432	7.37432	7.37432	21.95990	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-17.33531	-3.68716	-3.68716	-3.68716	-10.97995	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\sigma 1110)$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{\pi_2,MO}(\sigma 1110)$ (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$E_T(\sigma 1110)$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(\pi_2,MO)$ (eV)	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	-2.26759	-1.44915	-1.85836	-1.44915	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(\sigma 1)$ (eV)	-65.53833	-33.08452	-33.49373	-33.08452	-49.66493	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	43.0680	9.97851	16.4962	9.97851	25.2077	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	28.34813	6.56803	10.85807	6.56803	16.59214	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D$ (eV)	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kvib}$ (eV)	0.17897 [6]	0.15895 [7]	0.09931 [8]	0.09931 [8]	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{osc}$ (eV)	-0.25568	-0.08827	-0.16869	-0.11809	-0.07727	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(cmap)$ (eV)	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(\epsilon_4.\sigma 1110)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(\epsilon_5.\sigma 1110)$ (eV)	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(cmap)$ (eV)	7.51014	3.75498	4.39264	3.78480	7.83968	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.19. The total bond energies of alkenes calculated using the functional group composition and the energies of Table 15.18 compared to the experimental values [2]. The magnetic energy E_{magE} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by (15.58).

Formula	Name	C=C	C–C (i)	C–C (ii)	C–C (iii)	CH_2 (i)	CH_3	CH_2 (ii)	CH	C–C (a)	C–C (b)	C–C (c)	C–C (d)	C–C (e)	C–C (f)	E_{magE}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6	Propene	0	0	1	0	1	1	0	1	0	0	0	0	0	0	0	35.56033	35.63207	0.00201
C_4H_8	1-Butene	1	0	0	0	1	1	1	1	1	0	0	0	0	0	0	47.71803	47.78477	0.00140
C_4H_8	trans-2-Butene	1	0	2	0	0	2	0	2	0	0	0	0	0	0	0	47.93116	47.90395	-0.00057
C_4H_8	Isobutene	1	0	0	2	1	2	0	0	0	0	0	0	0	0	0	47.90314	47.96096	0.00121
C_5H_{10}	1-Pentene	1	0	1	0	1	1	2	1	1	0	0	0	0	0	0	59.87573	59.95094	0.00125
C_5H_{10}	trans-2-Pentene	1	0	2	0	0	2	1	2	1	0	0	0	0	0	0	60.08886	60.06287	-0.00043
C_5H_{10}	2-Methyl-1-butene	1	0	0	2	1	2	1	0	1	0	0	0	0	0	0	60.06084	60.09707	0.00060
C_5H_{10}	2-Methyl-2-butene	1	1	1	0	0	3	0	1	0	0	0	0	0	0	0	60.21433	60.16444	-0.00083
C_5H_{10}	3-Methyl-1-butene	1	0	1	0	1	3	0	2	0	2	0	0	0	0	0	59.97662	60.01727	0.00068
C_6H_{12}	1-Hexene	1	0	1	0	1	1	3	1	3	0	0	0	0	0	0	72.03343	72.12954	0.00133
C_6H_{12}	trans-2-Hexene	1	0	2	0	0	2	2	2	2	0	0	0	0	0	0	72.24656	72.23733	-0.00013
C_6H_{12}	trans-3-Hexene	1	0	2	0	0	2	2	2	2	0	0	0	0	0	0	72.24656	72.24251	-0.00006
C_6H_{12}	2-Methyl-1-pentene	1	0	0	2	1	2	2	0	2	0	0	0	0	0	0	72.21854	72.29433	0.00105
C_6H_{12}	2-Methyl-2-pentene	1	2	1	0	0	3	1	1	1	0	0	0	0	0	0	72.37203	72.37206	0.00000
C_6H_{12}	3-Methyl-1-pentene	1	0	1	0	1	2	1	2	1	2	0	0	0	0	0	72.13432	72.19173	0.00080
C_6H_{12}	4-Methyl-1-pentene	1	0	1	0	1	2	1	2	0	3	0	0	0	0	0	72.10599	72.21038	0.00145
C_6H_{12}	3-Methyl-trans-2-pentene	1	2	1	0	0	3	1	1	1	0	0	0	0	0	0	72.37203	72.33268	-0.00054
C_6H_{12}	4-Methyl-trans-2-pentene	1	0	2	0	0	3	0	3	0	2	0	0	0	0	0	72.34745	72.31610	-0.00043
C_6H_{12}	2-Ethyl-1-butene	1	0	0	2	1	2	2	0	4	0	0	0	0	0	0	72.21854	72.25909	0.00056
C_6H_{12}	2,3-Dimethyl-1-butene	1	0	0	2	1	3	0	1	0	2	0	0	0	0	0	72.31943	72.32543	0.00008
C_6H_{12}	3,3-Dimethyl-1-butene	1	0	1	0	1	3	0	1	0	0	3	0	0	0	-1	72.31796	72.30366	-0.00020
C_6H_{12}	2,3-Dimethyl-2-butene	1	4	0	0	0	4	0	0	0	0	0	0	0	0	0	72.49750	72.38450	-0.00156
C_7H_{14}	1-Heptene	1	0	1	0	1	1	4	1	4	0	0	0	0	0	0	84.19113	84.27084	0.00095
C_7H_{14}	5-Methyl-1-hexene	1	0	1	0	1	2	2	2	1	3	0	0	0	0	0	84.26369	84.30608	0.00050
C_7H_{14}	trans-3-Methyl-3-hexene	1	2	1	0	0	3	2	1	2	0	0	0	0	0	0	84.52973	84.42112	-0.00129
C_7H_{14}	2,4-Dimethyl-1-pentene	1	0	0	2	1	3	1	1	0	3	0	0	0	0	0	84.44880	84.49367	0.00053
C_7H_{14}	4,4-Dimethyl-1-pentene	1	0	1	0	1	3	1	1	0	0	4	0	0	0	0	84.27012	84.47087	0.00238
C_7H_{14}	2,4-Dimethyl-2-pentene	1	2	1	0	0	4	0	2	0	2	0	0	0	0	0	84.63062	84.54445	-0.00102
C_7H_{14}	trans-4,4-Dimethyl-2-pentene	1	0	2	0	0	4	0	2	0	0	3	0	0	0	-2	84.54076	84.54549	0.00006
C_7H_{14}	2-Ethyl-3-methyl-1-butene	1	0	0	2	1	3	1	1	1	2	0	0	0	0	0	84.47713	84.44910	-0.00033
C_7H_{14}	2,3,3-Trimethyl-1-butene	1	0	0	2	1	4	0	0	0	0	3	0	0	0	-2	84.51274	84.51129	-0.00002
C_8H_{16}	1-Octene	1	0	0	1	1	1	5	1	5	0	0	0	0	0	0	96.34883	96.41421	0.00068
C_8H_{16}	trans-2,2-Dimethyl-3-hexene	1	0	2	0	0	4	1	2	1	0	3	0	0	0	-2	96.69846	96.68782	-0.00011
C_8H_{16}	3-Ethyl-2-methyl-1-pentene	1	0	0	2	1	3	2	1	2	2	0	0	0	0	0	96.63483	96.61113	-0.00025
C_8H_{16}	2,4,4-Trimethyl-1-pentene	1	0	0	2	1	4	1	0	0	0	4	0	0	0	0	96.61293	96.71684	0.00107
C_8H_{16}	2,4,4-Trimethyl-2-pentene	0	2	1	0	0	5	0	1	0	0	3	0	0	0	-3	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	1	0	1	0	1	1	7	1	7	0	0	0	0	0	0	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	1	0	1	0	1	1	9	1	9	0	9	0	0	0	0	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	1	0	1	0	1	1	13	1	13	0	0	0	0	0	0	193.61043	193.71766	0.00055

Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of θ_c, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_3	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aC_c$ $(C_c(H)C_a=C_b)$	2.11323	2.86175	4.2895	-15.95954 C_a	9	-14.82575 C_c	1	0.85252	0.91771	0.75	1	0.75	1.07647	0				118.36	
$\angle C_cC_aC_c$ $(C_c(C_c)C_a=C_b)$	2.86175	2.86175	4.7958	-16.68411 C_c	24	-16.68411 C_c	24	0.81549	0.81549	1	1	1	0.81549	-1.85836				113.84	
$\angle C_bC_aC_c$ $(C_b=C_aC_c)$	2.53321	2.86175	4.7539	-16.88873 C_b	27	-16.68411 C_c	24	0.80561	0.81549	1	1	1	0.81055	-1.85836				123.46	124.4 (1,3,5-hexatriene CbCcCc) 121.7 (1,3,5-hexatriene CaCbCc) 124.4 (1,3-butadiene CCC) 125.3 (2-butene CbCaCc)
$\angle HC_aC_b$																118.36	123.46	118.19	
$\angle HC_aH$ $(H_2C_a=C_bC_c)$	2.04578	2.04578	3.4756	-15.95955	9	H	H	0.85252	1	1	1	0.75	1.17300	0				116.31	118.5 (2-methylpropene)
$\angle C_bC_aH$ $(H_2C_a=C_bC_c)$																116.31		121.85	121 (2-methylpropene)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYNES (C_nH_{2n-2}, $n=3,4,5...\infty$)

The straight and branched-chain alkynes, C_nH_{2n-2}, have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen atoms of acetylene. Based on the energy matching of the mutually bound C, these $C-C$-bond MOs are defined as primary and secondary $C-C$ functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal CH of a primary alkyne comprises a functional group that is solved equivalently to the methylyne group of acetylene as given in the Acetylene Molecule section.

The alkyl portion of the alkyne may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2 CH$) and t-butyl ($\left(CH_3\right)_3 C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C\equiv C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of acetylene, $-3.13026\,eV$, given by Eq. (14.342). $E_T\left(atom-atom,msp^3.AO\right)$ of each -alkyl-bond MO in Eq. (15.52) is $-1.85836\,eV$ or $-1.44915\,eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\,eV$ (Eq. (14.513), or methyl, $-0.72457\,eV$ (Eq. (14.151)), groups, respectively. For the $C-C$ groups each comprising a C single bond to $C\equiv C$, $E_T\left(atom-atom,msp^3.AO\right)$ is $-0.72457\,eV$ based on the energy match between the $C2sp^3$ HOs for the mutually bound C of the single and triple bonds. The parameter ω of each group is matched for oscillation in the transition state based on the group being primary or secondary.

The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.79-15.108) are given in Table 15.26. Each C of the $C \equiv C$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene.

Table 15.21. The symbols of functional groups of alkynes.

Functional Group	Group Symbol
CC triple bond	$C \equiv C$
C single bond to $C \equiv C$ (1°)	$C-C$ (i)
C single bond to $C \equiv C$ (2°)	$C-C$ (ii)
CH (terminal)	$C-H$ (i)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl)	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.22. The geometrical bond parameters of alkynes and experimental values [1].

Parameter	$C \equiv C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-H$ (i) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.28714	1.99185	1.99185	1.48719	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c\ (a_0)$	1.13452	1.41133	1.41133	0.99572	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c\ (\text{Å})$	1.20072	1.49369	1.49369	1.05383	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.203 (acetylene) 1.208 (2,4-hexadiyne)	1.450 (2,4-hexadiyne)	1.450 (2,4-hexadiyne)	1.060 (acetylene)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,c\ (a_0)$	0.60793	1.40557	1.40557	1.10466	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.88143	0.70855	0.70855	0.66953	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.23. The MO to HO intercept geometrical bond parameters of alkynes. E_T is $E_T\left(atom-atom, nsp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Carbon}\left(C2sp^3\right)$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RC_eC_bC_a-H$	C_a	-1.56513	0	0	0	-153.18082	0.91771	0.83008	-16.39088	-16.20002	90.99	89.01	48.71	0.98144	0.01428
$C_eC_a\equiv C_bH$	C_a	-1.56513	-0.36229	0	0	-153.54311	0.91771	0.81213	-16.75317	-16.56231	137.17	42.83	65.25	0.53890	0.59562
$C_eC_a\equiv C_bH$	C_b	-1.56513	0	0	0	-153.18082	0.91771	0.83008	-16.39088	-16.20002	137.91	42.09	66.24	0.51853	0.61599
$C_e-C_a\equiv C_bH$	C_e	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	75.71	104.29	35.59	1.61974	0.20841
$C-H\left(CH_3\right)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_2\right)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\left(CH\right)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_e-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_e-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_e-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.24. The energy parameters (eV) of functional groups of alkynes.

Parameters	$C \equiv C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-H$ (i) Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	3	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	1	1	0	0	1	1	0	0	0	1	1	0
c_4	6	2	2	1	1	1	1	2	2	2	2	2	2
c_5	0	0	0	1	3	2	1	0	0	0	0	0	0
C_{1a}	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2a}	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-182.53826	-31.29307	-31.29307	-40.62396	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	35.97770	9.64042	9.64042	13.66428	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	70.90876	7.85528	7.85528	13.65796	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-35.45438	-3.92764	-3.92764	-6.82898	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_{(MO/HO)}$ (eV)	-16.20002	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2,MO(MO/HO)}$ (eV)	0	-0.72457	-0.72457	-3.130269	0	0	0	0	0	0	0	0	0
$E_T(MO/HO)$ (eV)	-16.20002	-13.91032	-13.91032	-11.50462	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2,MO)$ (eV)	-94.90616	-31.63533	-31.63533	-31.63532	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-3.13026	-0.72457	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-98.03637	-32.35994	-32.35994	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	20.0186	10.3988	17.5426	30.8370	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	13.17659	6.84470	11.54682	20.29747	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.23468	-0.16749	-0.21754	-0.28197	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.27773 [9]	0.08989 [9]	0.08989 [9]	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{ave}$ (eV)	-0.09581	-0.12255	-0.17260	-0.10430	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{avg} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-98.02775	-32.48249	-32.53254	-31.73967	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial(e_1,MO/HO)}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial(e_1,MO/HO)}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	10.21841	3.21271	3.26276	3.50634	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.25. The total bond energies of alkynes calculated using the functional group composition and the energies of Table 15.24 compared to the experimental values [2].

Formula	Name	$C \equiv C$	$C-C$ (i)	$C-C$ (ii)	CH (i)	CH_3	CH_2	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_4	Propyne	1	1	0	1	1	0	0	0	0	0	0	0	0	29.42932	29.40432	-0.00085
C_4H_6	1-Butyne	1	1	0	1	1	1	0	1	0	0	0	0	0	41.58702	41.55495	-0.00077
C_4H_6	2-Butyne	1	0	2	0	2	0	0	0	0	0	0	0	0	41.72765	41.75705	0.00070
C_9H_{16}	1-Nonyne	1	1	0	1	1	6	0	6	0	0	0	0	0	102.37552	102.35367	-0.00021

Table 15.26. The bond angle parameters of alkynes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_1\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{C\,coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{C\,coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_c C_a C_b$ $\left(C_c C_a \equiv C_b H\right)$																		180	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_a C_b C_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_a C_b H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_a C_b C_c$															70.56			109.44	
$\angle C_a C_b H$															70.56			109.44	
$\angle C_b C_a C_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_b C_a H$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_a C_b H$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_b C_a C_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_b C_a C_d$															72.50			107.50	

ALKYL FLUORIDES ($C_nH_{2n+2-m}F_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl fluorides, $C_nH_{2n+2-m}F_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a fluorine. The $C-F$ bond comprises a functional group for each case of F replacing a H of methane in the series $H_{4-m}C-F_m$, $m=1,2,3,4$, and F replacing a H of an alkane. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-F$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the F AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\,eV$ (Eq. (15.25)), and the F AO has an energy of $E\left(F\right)=-17.42282\,eV$. To meet the equipotential condition of the union of the $C-F$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-F$-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO\ to\ F\right)=\frac{E\left(C,2sp^3\right)}{E\left(F\right)}c_2\left(C2sp^3HO\right)=\frac{-14.63489\,eV}{-17.42282\,eV}\left(0.91771\right)=0.77087 \quad (15.110)$$

$E_{\gamma}\left(atom-atom,msp^3.AO\right)$ of the $C-F$-bond MO in Eq. (15.52) based on the charge donation from F to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the F atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl fluorides are

given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). In the case of trifluoromethane, E_{mag} is positive since the term due to the fluorine atoms cancels that of the CH group. The $C-C$ bonds to the CHF group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CF group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.110) are given in Table 15.32.

Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

Functional Group	Group Symbol
CF of CF_mH_{4-m}	$C-F$ (i)
CF of $C_nH_{2n+2-m}F_m$	$C-F$ (ii)
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.28. The geometrical bond parameters of branched-chain alkyl fluorides and experimental values [1].

Parameter	$C-F$ (i) Group	$C-F$ (ii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.72139	1.72139	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.31202	1.31202	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.38858	1.38858	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.382 (methyl fluoride)	1.382 (methyl fluoride)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,c\ (a_0)$	1.11435	1.11435	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.76219	0.76219	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.29. The MO to HO intercept geometrical bond parameters of branched-chain alkyl fluorides. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\ (a_0)$	$d_2\ (a_0)$
$H_{4-m}C_u-F_m$ (C_u-F (i))	C_u	-1.34946	0	0	0	-152.96515	0.91771	0.84115	-16.17521	-15.98435	100.77	79.23	47.86	1.15488	0.15714
$H_{4-m}C_u-F_m$ (C_u-F (i))	F	-1.34946	0	0	0		0.78069	0.84115	-16.17521		100.77	79.23	47.86	1.15488	0.15714
$-H_2C_hC_uF$ (C_u-F (ii))	C_u	-1.34946	-0.92918	0	0	-153.89433	0.91771	0.79546	-17.10440	-16.91353	97.02	82.98	45.11	1.21483	0.09718
$-H_2C_hC_uF$ (C_u-F (ii))	F	-1.34946	0	0	0		0.78069	0.84115	-16.17521		100.77	79.23	47.86	1.15488	0.15714
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_uC_hH_2CH_2-$ ($C-C$ (a))	C_u	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_uC_hH_2CH_2-$ ($C-C$ (a))	C_h	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_uC_h\left(H_2C_e-R'\right)HCH_2-$ ($C-C$ (b))	C_h	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_u\left(R'-H_2C_d\right)C_h\left(R''-H_2C_e\right)CH_2-$ ($C-C$ (c))	C_h	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_uC_h\left(H_2C_e-R'\right)HCH_2-$ ($C-C$ (d))	C_h	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_u\left(R'-H_2C_d\right)C_h\left(R''-H_2C_e\right)CH_2-$ ($C-C$ (e))	C_h	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_uC_h\left(H_2C_e-R'\right)HCH_2-$ ($C-C$ (f))	C_h	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_u\left(R'-H_2C_d\right)C_h\left(R''-H_2C_e\right)CH_2-$ ($C-C$ (f))	C_h	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.30. The energy parameters (eV) of functional groups of branched-chain alkyl fluorides.

Parameters	$C-F$ (i) Group	$C-F$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.77087	0.77087	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
$C_{1\sigma}$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{2\sigma}$	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-32.02108	-32.02108	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	10.37015	10.37015	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	9.30097	9.30097	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-4.65048	-4.65048	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E_1(no\ mo)$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(no\ mo)$ (eV)	0	0	0	0	0	0	0	0	0	0	0
$E_T(no\ mo)$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-31.63534	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, mxp^3.AO)$ (eV)	-2.69892	-2.69892	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-34.33429	-34.33429	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	24.8506	12.9435	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	16.35707	8.51966	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D$ (eV)	-0.27472	-0.19826	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kvib}$ (eV)	0.13849 [10]	0.10911 [11]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{osc}$ (eV)	-0.20547	-0.14371	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-34.53976	-34.47800	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(e_1.no\ mo)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(e_2.no\ mo)$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	5.26998	5.20822	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.31. The total bond energies of branched-chain alkyl fluorides calculated using the functional group composition and the energies of Table 15.30 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-F$ (i)	$C-F$ (ii)	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF_4	Tetrafluoromethane	4	0	0	0	0	0	0	0	0	0	0	0	21.07992	21.016	-0.00303
CHF_3	Trifluoromethane	3	0	0	0	1	0	0	0	0	0	0	1	19.28398	19.362	0.00405
CH_2F_2	Difluoromethane	2	0	0	1	0	0	0	0	0	0	0	0	18.37012	18.280	-0.00496
C_3H_7F	1-Fluoropropane	0	1	1	2	0	2	0	0	0	0	0	-1	41.86745	41.885	0.00041
C_3H_7F	2-Fluoropropane	0	1	2	0	1	0	2	0	0	0	0	-1	41.96834	41.963	-0.00012

Table 15.32. The bond angle parameters of branched-chain alkyl fluorides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle FC_aF$ (C_a-F (i))	2.62403	2.62403	4.3128	-16.17521 F	12	-16.17521 F	12	0.84115	0.84115	1	1	1	0.84115	-1.44915				110.53	108.8 (fluoroform)
$\angle HC_aF$ (C_a-F (i))	2.11106	2.62403	3.8987	-17.10440 C_a	31	-17.42282 F	F	0.79546	0.78092 (Eq. (15.64))	0.75	1	0.75	0.98172	0				110.38	
$\angle C_bC_aF$ (C_a-F (ii))	2.91547	2.62403	4.5826	-16.68412 C_b	25	-17.42282 F	F	0.81549	0.77087 (Eq. (15.110))	1	1	1	0.79318	-1.85836				111.53	110.3 (1,2-difluoroethane)
$\angle C_bC_aH$ (C_a-F (ii))	2.91547	2.11106	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.83	111.0 (1,1-difluoroethane)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H		0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H		0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL CHLORIDES ($C_nH_{2n+2-m}Cl_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl chlorides, $C_nH_{2n+2-m}Cl_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a chlorine. The $C-Cl$ bond comprises a functional group for each case of Cl replacing a H of methane for the series $H_{4-m}C-Cl_m$, $m=1,2,3$, with the $C-Cl$ bond of CCl_4 comprising another functional group due to the limitation of the minimum energy of Cl matched to that of the $C2sp^3$ HO. In addition, the $C-Cl$ bond due to Cl replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-Cl$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the Cl AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chorine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\,eV$ (Eq. (15.25)), and the Cl AO has an energy of $E\left(Cl\right)=-12.96764\,eV$. To meet the equipotential condition of the union of the $C-Cl$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-Cl$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ Cl\right)=\frac{E(Cl)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-12.96764\,eV}{-14.63489\,eV}(0.91771)=0.81317 \quad (15.110)$$

The valence energy of the carbon $2p$ is $-11.2603\,eV$ and that of the Cl AO is $-12.96764\,eV$. The energy difference is more than that of $2E_T\left(C-C,2sp^3\right)$ given by Eq. (14.151) for a single

bond. Thus, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-Cl$-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is $-1.44915\,eV$ based on the energy match between the $C2sp^3$ HO and the Cl AO corresponding to the energy contributions equivalent to those of methyl groups, $-0.72457\,eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The $C-C$ bonds to the $CHCl$ group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CCl group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.38.

Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

Functional Group	Group Symbol
CCl of CCl_mH_{4-m}	$C-Cl$ (i)
CCl of CCl_4	$C-Cl$ (ii)
CCl of $C_nH_{2n+2-m}Cl_m$	$C-Cl$ (iii)
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.34. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

Parameter	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-Cl$ (iii) Group	$C-H\left(CH_3\right)$ Group	$C-H\left(CH_2\right)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\left(a_0\right)$	2.32621	2.37026	2.32621	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\left(a_0\right)$	1.69136	1.70729	1.69136	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\left(\AA\right)$	1.79005	1.80692	1.79005	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $\left(\AA\right)$	1.785 (methyl chloride)	1.767 (carbon tetrachloride)	1.802 (ethyl chloride) 1.790 (1,2-dichloroethane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\left(a_0\right)$	1.59705	1.64416	1.59705	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.72709	0.72030	0.72709	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.35. The MO to HO intercept geometrical bond parameters of branched-chain alkyl chlorides. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{united}\left(a_0\right)$	$r_{fixed}\left(a_0\right)$	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\left(a_0\right)$	$d_2\left(a_0\right)$
$H_{4-m}C'_a-Cl_m$, $m=1,2,3$, (C'_a-Cl (i))	C'_a	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	69.62	110.38	30.90	1.99599	0.30463
$H_{4-m}C'_a-Cl_m$, $m=1,2,3$, (C'_a-Cl (i))	Cl	-0.72457	0	0	0		1.05158	0.87495	-15.55033		69.62	110.38	30.90	1.99599	0.30463
C'_aCl_4 (C'_a-Cl (ii))	C'_a	-0.46459	0	0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	66.98	113.02	29.87	2.05530	0.34801
C'_aCl_4 (C'_a-Cl (ii))	Cl	-0.46459	0	0	0		1.05158	0.88983	-15.29034		66.98	113.02	29.87	2.05530	0.34801
$-H_2C'_bC'_a-Cl$ (C'_a-Cl (iii))	C'_a	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	63.18	116.82	27.48	2.06384	0.37248
$-H_2C'_bC'_a-Cl$ (C'_a-Cl (iii))	Cl	-0.72457	0	0	0		1.05158	0.87495	-15.55033		69.62	110.38	30.90	1.99599	0.30463
$C'-H\left(C'H_3\right)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\left(C'H_2\right)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\left(C'H\right)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2C'H_2-$ ($C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2C'H_2-$ ($C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ ($C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ ($C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ ($C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ ($C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ ($C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ ($C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.36. The energy parameters (eV) of functional groups of branched-chain alkyl chlorides.

Parameters	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-Cl$ (iii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.81317	0.81317	0.81317	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	1	1	0	1	1	0	0	0	1	1	0
c_4	2	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.81317	0.81317	0.81317	1	1	1	1	1	1	1	1	1
V_e (eV)	-29.68411	-28.95265	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	8.04432	7.96922	8.04432	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	6.38036	6.10748	6.38036	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ni} (eV)	-3.19018	-3.05374	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\text{no nu})$ (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2NO}(\text{no nu})$ (eV)	-1.44915	-0.92918	-1.44915	0	0	0	0	0	0	0	0	0
$E_T(\text{no nu})$ (eV)	-13.18574	-13.70571	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2NO)$ (eV)	-31.63536	-31.63540	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-1.44915	-0.92918	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(\text{nu})$ (eV)	-33.08452	-32.56455	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	7.42995	7.22380	13.0612	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_g (eV)	4.89052	4.75483	8.59708	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{ij}$ (eV)	-0.14475	-0.14048	-0.19191	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Keb}$ (eV)	0.08059 [12]	0.08059 [12]	0.09113 [13]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{coz}$ (eV)	-0.10445	-0.10019	-0.14635	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(\text{image})$ (eV)	-33.18897	-32.66473	-33.23086	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(\text{no nu})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(\text{no nu})$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{ij}(\text{image})$ (eV)	3.77116	3.39496	3.96108	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.37. The total bond energies of branched-chain alkyl chlorides calculated using the functional group composition and the energies of Table 15.36 compared to the experimental values [2]. The magnetic energy E_{mg} that is subtracted from the weighted sum of the $E_D(kcal/mol)$ (eV) values based on composition is given by (15.58).

Formula	Name	C–Cl (i)	C–Cl (ii)	C–Cl (iii)	CH_3	CH_2	CH (i)	CH (ii)	C–C (a)	C–C (b)	C–C (c)	C–C (d)	C–C (e)	C–C (f)	E_{mg}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CCl_4	Tetrachloromethane	0	0	4	0	0	0	0	0	0	0	0	0	0	-1	13.43181	13.448	0.00123
$CHCl_3$	Trichloromethane	3	0	0	0	0	1	0	0	0	0	0	0	0	-1	14.49146	14.523	0.00217
CH_2Cl_2	Dichloromethane	2	0	0	0	1	0	0	0	0	0	0	0	0	0	15.37248	15.450	0.00499
CH_3Cl	Chloromethane	1	0	0	1	0	0	0	0	0	0	0	0	0	0	16.26302	16.312	0.00299
C_2H_5Cl	Chloroethane	0	0	1	1	1	0	0	0	1	0	0	0	0	0	28.61064	28.571	-0.00138
C_3H_7Cl	1-Chloropropane	0	0	1	1	2	0	0	2	0	0	0	0	0	0	40.76834	40.723	-0.00112
C_3H_7Cl	2-Chloropropane	0	0	1	2	0	1	0	0	2	0	0	0	0	0	40.86923	40.858	-0.00028
C_4H_9Cl	1-Chlorobutpane	0	0	1	1	3	0	0	3	0	0	0	0	0	0	52.92604	52.903	-0.00044
C_4H_9Cl	2-Chlorobutane	0	0	1	2	1	1	0	1	2	0	0	0	0	0	52.02693	52.972	-0.00104
C_4H_9Cl	1-Chloro-2-methylpropane	0	0	1	2	1	1	0	0	3	0	0	0	0	0	52.99860	52.953	-0.00085
C_4H_9Cl	2-Chloro-2-methylpropane	0	0	1	3	0	0	0	0	0	3	0	0	0	-1	53.21057	53.191	-0.00037
$C_5H_{11}Cl$	1-Chloropentane	0	0	1	1	4	0	0	4	0	0	0	0	0	0	65.08379	65.061	0.00034
$C_5H_{11}Cl$	1-Chloro-3-methylbutane	0	0	1	2	2	1	0	1	3	0	0	0	0	0	65.15630	65.111	-0.00069
$C_5H_{11}Cl$	2-Chloro-2-methylbutane	0	0	1	3	1	0	0	1	0	3	0	0	0	-1	65.36827	65.344	-0.00037
$C_5H_{11}Cl$	2-Chloro-3-methylbutane	0	0	1	3	0	2	0	0	3	0	1	0	0	0	65.16582	65.167	0.00002
$C_6H_{13}Cl$	2-Chlorohexane	0	0	1	2	3	1	0	3	2	0	0	0	0	0	77.34233	77.313	-0.00038
$C_8H_{17}Cl$	1-Chlorooctane	0	0	1	1	7	0	0	7	0	0	0	0	0	0	101.55684	101.564	0.00007
$C_{12}H_{25}Cl$	1-Chlorododecane	0	0	1	1	11	0	0	11	0	0	0	0	0	0	150.87640	150.202	0.00009
$C_{18}H_{37}Cl$	1-Chlorooctadecane	0	0	1	1	7	0	0	7	0	0	0	0	0	0	223.13384	223.175	0.00018

Table 15.38. The bond angle parameters of branched-chain alkyl chlorides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_n)	$2c'$ Bond 2 (a_n)	$2c'$ Terminal Atoms (a_n)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	a_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle ClC_aCl$ (C_a-Cl (i))	3.38271	3.38271	5.5889	-14.82575 Cl	1	-14.82575 Cl	1	0.91771	0.91771	1	0.81317 (Eq. 15.111)	1	0.91771	-0.92918				111.40	112.0 (dichloromethane) 111.3 (chloroform)
$\angle HC_aCl$ (C_a-Cl (iii))	2.11106	3.38271	4.5961	-16.27490 C_a	15	-12.96764 Cl	Cl	0.83600	0.91771	0.75	0.95310 (Eq. 15.65))	0.75	1.09775	0				111.46	
$\angle HC_aH$ $\angle HC_bH$ (C_a-Cl (iii))	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	109.2 ($\angle HC_aH$ ethyl chloride) 109.8 ($\angle HC_bH$ ethyl chloride)
$\angle C_aC_bH_b$ (C_a-Cl (iii))															70.56			109.44	
$\angle C_bC_aCl$ (C_a-Cl (iii))	2.91547	3.38271	5.1539	-15.75493 C_b	7	-12.96764 Cl	Cl	0.86359	0.86359	1	0.81317 (Eq. 15.111)	1	0.86359	-0.92918				109.61	110.7 (ethyl chloride) 111.0 (1,1-dichloroethane) 109.0 (1,2-dichloroethane) 109.6 (1,1,1-trichloroethane) 110.0 (hexachloroethane)
$\angle C_bC_aH_a$ (C_a-Cl (iii))	2.91547	2.11106	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.83	110.6 (ethyl chloride)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ ten C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_a$															72.50			107.50	

ALKYL BROMIDES ($C_nH_{2n+2-m}Br_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl bromides, $C_nH_{2n+2-m}Br_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a bromine. The $C-Br$ bond comprises a functional group for each case of Br replacing a H of methane for the series $H_{4-m}C-Br_m$, $m=1,2,3$, with the $C-Br$ bond of CBr_4 comprising another functional group due to the limitation of the minimum energy of Br matched to that of the $C2sp^3$ HO. In addition, the $C-Br$ bond due to Br replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-Br$ functional groups comprises the hybridization of the $2s$ and $2p$ shells of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ hybridized orbital (HO) and the Br AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), and the Br AO has an energy of $E\left(Br\right)=-11.81381\ eV$. To meet the equipotential condition of the union of the $C-Br$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-Br$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ Br\right)=\frac{E(Br)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-11.81381\ eV}{-14.63489\ eV}(0.91771)=0.74081 \quad (15.112)$$

The valence energy of the carbon $2p$ is $-11.2603\ eV$ and that of the Br AO is $-11.81381\ eV$. The energy difference is less than that of $E_T\left(C-C,2sp^3\right)$ given by Eq. (14.151) for a single bond. Thus, $E_T\left(atom-atom,msp^3.AO\right)$ of the alkyl $C-Br$-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is $-0.92918\ eV$ (Eq. (14.513) based on the maximum single-bond-energy contribution of the $C2sp^3$ HO. $E_T\left(atom-atom,msp^3.AO\right)$ of the series CBr_mH_{4-m} $m=1,2,3$ is equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)). For CBr_4, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-Br$-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is $-0.36229\ eV$ (Eqs. (15.18-15.20 and Eq, (15.29) with a linear combination of $s=1$, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ and $E_T\left(atom-atom,msp^3.AO\right)=0$) based on the maximum charge density on the $C2sp^3$ HO.

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl bromides are given in Tables 15.40, 15.41, and 15.42, respectively. The total energy of each branched-chain alkyl bromide given in Table 15.43 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.42 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The $C-C$ bonds to the $CHBr$ group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CBr group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} is subtracted for each t-butyl group. In the case of 2,3-dibromo-2-methylbutane, E_{mag} is positive since the terms due to the two bromine atoms cancel that of the t-butyl and CH groups. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.112) are given in Table 15.44.

Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

Functional Group	Group Symbol
CBr of CBr_mH_{4-m}	$C-Br$ (i)
CBr of CBr_4	$C-Br$ (ii)
CBr of $C_nH_{2n+2-m}Br_m$	$C-Br$ (iii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.40. The geometrical bond parameters of branched-chain alkyl bromides and experimental values [1].

Parameter	$C-Br$ (i) Group	$C-Br$ (ii) Group	$C-Br$ (iii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.49163	2.52509	2.47329	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.83395	1.84622	1.82719	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (A)$	1.94097	1.95396	1.93381	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.933 (methyl bromide)	1.935 (carbon tetrabromide)	1.93 (1,1,1-tribromoethane) 1.950 (1,2-dibromoethane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.68667	1.72265	1.66689	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.73604	0.73115	0.73877	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.41. The MO to HO intercept geometrical bond parameters of branched-chain alkyl bromides. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $(C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$H_{3-m}(C_a-Br_m,\ m=1,2,3.$ $(C_a-Br$ (i))	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	68.10	111.90	29.52	2.16808	0.33413
$H_{3-m}C_a-Br_m,\ m=1,2,3.$ $(C_a-Br$ (i))	Br	-0.36229	0	0	0		1.15169	0.89582	-15.18804		68.10	111.90	29.52	2.16808	0.33413
C_aBr_4 $(C_a-Br$ (ii))	C_a	-0.18114	0	0	0	-151.79683	0.91771	0.90664	-15.00689	-14.81603	66.10	113.90	28.76	2.21357	0.36734
C_aBr_4 $(C_a-Br$ (ii))	Br	-0.18114	0	0	0		1.15169	0.90664	-15.00689		66.10	113.90	28.76	2.21357	0.36734
$-H_2C_bC_aBr$ $(C_a-Br$ (iii))	C_a	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21952	-16.02866	62.67	117.33	26.55	2.21237	0.38518
$-H_2C_bC_aBr$ $(C_a-Br$ (iii))	Br	-0.46459	0	0	0		1.15169	0.88983	-15.29034		69.19	110.81	29.93	2.14337	0.31618
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R''-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.42. The energy parameters (eV) of functional groups of branched-chain alkyl bromides.

Parameters	$C-Br$ (i) Group	$C-Br$ (ii) Group	$C-Br$ (iii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.74081	0.74081	0.74081	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	0.74081	0.74081	0.74081	1	1	1	1	1	1	1	1	1
V_s (eV)	-27.94806	-27.44996	-28.22940	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	7.41885	7.36953	7.44631	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	5.60839	5.43544	5.70686	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{sp} (eV)	-2.80419	-2.71772	-2.85343	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E\{sp\ no\}$ (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{sp^3,M}\{sp\ no\}$ (eV)	-0.72457	-0.36229	-0.92918	0	0	0	0	0	0	0	0	0
$E_T\{sp\ no\}$ (eV)	-13.91032	-14.27260	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T\{sp^3M\}$ (eV)	-31.63533	-31.63531	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-0.72457	-0.36229	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T\{sp\}$ (eV)	-32.35994	-31.99766	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	6.39733	6.27059	6.46864	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	4.21083	4.12741	4.25777	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{ES}$ (eV)	-0.13137	-0.12861	-0.13293	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kab}$ (eV)	0.07575 [14]	0.08332 [15]	0.07575 [14]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{exc}$ (eV)	-0.09349	-0.08695	-0.09506	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T\{virsp\}$ (eV)	-32.45343	-32.08460	-32.65961	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{mfval}\{s,sp\ no\}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{mfval}\{s,sp\ no\}$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D\{virsp\}$ (eV)	3.18365	2.81482	3.38983	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.43. The total bond energies of branched-chain alkyl bromides calculated using the functional group composition and the energies of Table 15.42 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-Br$ (i)	$C-Br$ (ii)	$C-Br$ (iii)	CH_3	CH_2	CH (i)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CBr_4	Tetrabromomethane	0	4	0	0	0	0	0	0	0	0	0	0	0	-1	11.25929	11.196	-0.00566
$CHBr_3$	Tribromomethane	3	0	0	0	0	1	0	0	0	0	0	0	0	0	12.87698	12.919	0.00323
CH_3Br	Bromomethane	1	0	0	1	0	0	0	0	0	0	0	0	0	0	15.67551	15.732	0.00360
C_3H_7Br	1-Bromopropane	0	0	1	1	1	0	0	1	0	0	0	0	0	0	28.03939	27.953	-0.00308
C_3H_7Br	2-Bromopropane	0	0	1	1	2	0	0	2	0	0	0	0	0	0	40.19709	40.160	-0.00093
$C_5H_{10}Br_2$	2,3-Dibromo-2-methylbutane	1	0	0	3	0	1	0	0	2	0	0	0	0	0	40.29798	40.288	-0.00024
$C_6H_{13}Br$	1-Bromohexane	0	0	1	1	5	0	0	5	0	0	0	0	2	0	68.48143	68.477	-0.00007
$C_7H_{15}Br$	1-Bromoheptane	0	0	1	1	6	0	0	6	0	0	0	0	0	0	76.67019	76.634	-0.00047
$C_8H_{17}Br$	1-Bromooctane	0	0	1	1	7	0	0	7	0	0	0	0	0	0	88.82789	88.783	0.00051
$C_{12}H_{25}Br$	1-Bromododecane	0	0	1	1	11	0	0	11	0	0	0	0	0	0	100.98559	100.952	-0.00033
$C_{16}H_{33}Br$	1-Bromohexadecane	0	0	1	1	15	0	0	15	0	0	0	0	0	0	149.61639	149.573	-0.00029
																198.24719	198.192	-0.00028

Table 15.44. The bond angle parameters of branched-chain alkyl bromides and experimental values [1]. In the calculation of θ_e, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (σ_n)	$2c'$ Bond 2 (σ_n)	$2c'$ Terminal Atoms (σ_n)	$E_{Centralatom}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Centralatom}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle BrC_aBr$ (C_a-Br (i))	3.66790	3.66790	6.0816	-15.18804 Br	2	-15.18804 Br	2	0.89582	0.89582	1	0.74081 (Eq. (15.112))	1	0.89582	-0.92918				112.00	111.2 (methyl bromide) 113.2 (dibromomethane) 111.7 (bromoform)
$\angle HC_aBr$ (C_a-Br (iii))	2.11106	3.66790	4.8312	-15.55033 C_a	5	-11.81381 Br	Br	0.87495	0.91771	0.75	0.86829 (Eq. (15.65))	0.75	1.04887	0				110.53	109 (dibromomethane)
$\angle HC_aH$ $\angle HC_aH$ (C_a-Br (iii))	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bH_b$ (C_a-Br (iii))															70.56			109.44	110 (1,2-dibromoethane) 109.0 (1,1,1-tribromoethane)
$\angle C_aC_aBr$ (C_a-Br (iii))	2.91547	3.65437	3.4247	-15.75493 C_b	7	-11.81381 Br	Br	0.86359	0.86359	1	0.74081 (Eq. (15.112))	1	0.86359	-0.72457				110.82	109.5 (1,1-dibromoethane)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL IODIDES ($C_nH_{2n+2-m}I_m$, $n=1,2,3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkyl iodides, $C_nH_{2n+2-m}I_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by an iodine atom. The $C-I$ bond comprises a functional group for I replacing a H of methane (CH_3I) or for I replacing a H of an alkane corresponding to the series $C_nH_{2n+2-m}I_m$. The $C-I$ bond of each of CH_2I_2 and CHI_3 comprise separate functional groups due to the limitation of the minimum energy of I matched to that of the $C2sp^3$ HO. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the $C-I$ functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the I AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)). The I AO has an energy of $E\left(I\right)=-10.45126\ eV$. To meet the equipotential condition of the union of the $C-I$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.51) for the $C-I$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ I\right)=\frac{E(I)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-10.45126\ eV}{-14.63489\ eV}(0.91771)=0.65537 \quad (15.113)$$

The valence energy of the carbon $2p$ is $-11.2603\ eV$ and that of the I AO is $-10.45126\ eV$. The energy difference is positive. Thus, based on the maximum charge density on the $C2sp^3$

HO $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-I$-bond MO in Eq. (15.52) due to the charge donation from the C and I atoms to the MO is $-0.36229\,eV$ (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of $s=1$, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\,eV$ and $E_T\left(atom-atom,msp^3.AO\right)=0$) for methyl and alkyl iodides, $-0.18114\,eV$ for diiodomethane, and 0 for CHI_3.

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl iodides are given in Tables 15.46, 15.47, and 15.48, respectively. The total energy of each branched-chain alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The $C-C$ bonds to the CHI group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CI group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.113) are given in Table 15.50.

Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

Functional Group	Group Symbol
CI of CH_3I and $C_nH_{2n+2-m}I_m$	$C-I$ (i)
CI of CH_2I_2	$C-I$ (ii)
CI of CHI_3	$C-I$ (iii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.46. The geometrical bond parameters of branched-chain alkyl iodides and experimental values [1].

Parameter	$C-I$ (i) Group	$C-I$ (ii) Group	$C-I$ (iii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.67103	2.68865	2.70662	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	2.01881	2.02546	2.03222	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	2.13662	2.14365	2.15081	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	2.132 (methyl iodide)	2.132 (methyl iodide)	2.15 (carbon tetraiodide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c\ (a_0)$	1.74894	1.76815	1.78770	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.75582	0.75334	0.75083	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.47. The MO to HO intercept geometrical bond parameters of branched-chain alkyl iodides. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
CH_3I $(C_a-I$ (i))	C_a	-0.18114	0	0	0	-151.79683	0.91771	0.90664	-15.00689	-14.81603	69.63	110.37	29.08	2.33442	0.31560
CH_3I $(C_a-I$ (i))	I	-0.18114	0	0	0		1.30183	0.90664	-15.00689		69.63	110.37	29.08	2.33442	0.31560
$-H_2C_bC_aI$ $(C_a-I$ (i))	C_a	-0.18114	-0.92918	0	0	-152.72602	0.91771	0.85377	-15.93608	-15.74521	63.16	116.84	25.82	2.40436	0.38554
$-H_2C_bC_aI$ $(C_a-I$ (i))	I	-0.18114	0	0	0		1.30183	0.90664	-15.00689		69.63	110.37	29.08	2.33442	0.31560
$C_aH_2I_2$ $(C_a-I$ (ii))	C_a	-0.09057	0	0	0	-151.70626	0.91771	0.91214	-14.91632	-14.72546	68.61	111.39	28.71	2.35818	0.33272
$C_aH_2I_2$ $(C_a-I$ (ii))	I	-0.09057	0	0	0		1.30183	0.91214	-14.91632		68.61	111.39	28.71	2.35818	0.33272
C_aHI_3 $(C_a-I$ (iii))	C_a	0	0	0	0	-151.61569	0.91771	0.91771	-14.82575	-14.63489	67.56	112.44	28.32	2.38256	0.35035
C_aHI_3 $(C_a-I$ (iii))	I	0	0	0	0		1.30183	0.91771	-14.82575	-14.63489	67.56	112.44	28.32	2.38256	0.35035
$C-H\left(CH_3\right)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_2\right)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\left(CH\right)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.48. The energy parameters (eV) of functional groups of branched-chain alkyl iodides.

Parameters	$C-I$ (i) Group	$C-I$ (ii) Group	$C-I$ (iii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.65537	0.65537	0.65537	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	1	0	1	1	0	0	0	1	1	0
c_4	2	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1n}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2n}	0.65537	0.65537	0.65537	1	1	1	1	1	1	1	1	1
V_r (eV)	-26.59109	-26.34902	-26.10696	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	6.73951	6.71739	6.69505	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	4.97768	4.90005	4.82280	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ss} (eV)	-2.48884	-2.45002	-2.41140	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\lambda\sigma\ n\sigma)$ (eV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2,MO}(\lambda\sigma\ n\sigma)$ (eV)	-0.36229	-0.18114	0	0	0	0	0	0	0	0	0	0
$E_T(\lambda\sigma\ n\sigma)$ (eV)	-14.29907	-14.45375	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2\lambda\sigma)$ (eV)	-31.63534	-31.63535	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-0.36229	-0.18114	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(\lambda\sigma)$ (eV)	-31.99766	-31.81651	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	10.2318	5.36799	9.90080	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	6.73472	3.53331	6.51688	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{D}$ (eV)	-0.16428	-0.11832	-0.15977	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Krab}$ (eV)	0.06608 [16]	0.06608 [16]	0.06608 [16]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{mc}$ (eV)	-0.13124	-0.08527	-0.12673	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-32.12889	-31.90179	-31.76210	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_1\ AO:n\sigma)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_2\ AO:n\sigma)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	2.71108	2.63201	2.34429	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.49. The total bond energies of branched-chain alkyl iodides calculated using the functional group composition and the energies of Table 15.48 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) val based on composition is given by (15.58).

Formula	Name	$C-I$ (i)	$C-I$ (ii)	$C-I$ (iii)	CH_3	CH_2	CH (i)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CHI_3	Triiodomethane	0	0	3	0	0	1	0	0	0	0	0	0	0	0	10.35888	10.405	0.00444
CH_2I_2	Diiodomethane	0	2	0	0	1	0	0	0	0	0	0	0	0	-1	12.94614	12.921	-0.00195
CH_3I	Iodomethane	1	0	0	1	0	0	0	0	0	0	0	0	0	0	15.20294	15.163	-0.00263
C_2H_5I	Iodoethane	1	0	0	1	1	0	0	1	0	0	0	0	0	0	27.36064	27.343	-0.00066
C_3H_7I	1-Iodopropane	1	0	0	1	2	0	0	2	0	0	0	0	0	0	39.51834	39.516	-0.00006
C_3H_7I	2-Iodopropane	1	0	0	2	0	1	0	0	2	0	0	0	0	0	39.61923	39.623	0.00009
C_4H_9I	2-Iodo-2-methylpropane	1	0	0	3	0	0	0	0	0	3	0	0	0	-1	51.96057	51.899	-0.00119

Table 15.50. The bond angle parameters of branched-chain alkyl iodides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, nsp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle IC_aI$ (C_a-I (ii))	4.05092	4.05092	6.7205	-10.45126 I	1	-10.45126 I	1	1	1	1	0.65537 (Eq. (15.113))	1	1	-0.36228				112.10	
$\angle HC_aI$ (C_a-I (i))	2.11106	4.03763	5.2203	-14.82575 C_a	1	-10.45126 I	1	0.91771	0.91771	0.75	0.76815 (Eq. (15.65))	0.75	1.00000	0				112.39	
$\angle HC_aH$ $\angle HC_bH$ (C_a-I (i))	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	111.2 (methyl iodide)
$\angle C_aC_bH_b$ (C_a-I (i))															70.56			109.44	
$\angle C_bC_aI$ (C_a-I (i))	2.91547	4.03763	5.7939	-15.55033 C_b	5	-10.45126 I	1	0.87495	0.87495	1	0.65537 (Eq. (15.113))	1	0.87495	-0.36228				111.86	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKENYL HALIDES ($C_nH_{2n-m}X_m$, $n=3,4,5...\infty$ $m=1,2,3...\infty$)

The branched-chain alkenyl halides, $C_nH_{2n+2-m}X_m$ with $X=F,Cl,Br,I$, may comprise alkyl and alkenyl functional groups wherein at least one H is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl H, the $C-X$ bond comprises the alkyl-halogen functional groups given in their respective sections. The alkenyl halogen $C-X$ bond comprises a separate functional group for each case of X bonding to the $C=C$-bond functional group given in the Alkenes section. In addition the CH group of the moiety $XCH=C$ comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes, C_nH_{2n}, comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are C vinyl single bond to $-C(C)=C$, C vinyl single bond to $-C(H)=C$, and C vinyl single bond to $-C(C)=CH_2$. In addition, CH_2 of the $-C=CH_2$ moiety is also an alkene functional group solved in the Alkenes section.

Consider the case where $X=Cl$ substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct $C-Cl$ functional groups can be identified: Cl vinyl single bond to $-C(C)=C$ and Cl vinyl single bond to $-C(H)=C$. The alkenyl-halide CH group is equivalent to that solved in the Hydrogen Carbide (CH) section except that $\Delta E_{H_2MO}(AO/HO)=-1.13379\ eV$ in order to energy match to the $C-Cl$ and $C=C$ bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759\,eV$, given by Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.52) is $-1.85836\,eV$ or $-1.44915\,eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918\,eV$ (Eq. (14.513), or methyl, $-0.72457\,eV$ (Eq. (14.151)), groups, respectively.

The solution of each $C-X$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. The alkenyl $C-X$-bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the $C-X$-bond MO are each energy matched to the alkene $C2sp^3$ HO. In alkenyl halides with $X=Cl,Br,\ or\ I$, the energy of the halogen atom is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. For example, the hybridization factor C_2 of Eq. (15.52) for the alkenyl $C-Cl$-bond MO given by Eq. (15.111) is $C_2\left(C2sp^3HO\ to\ \mathrm{Cl}\right)=0.81317$.

$E_T\left(atom-atom,msp^3.AO\right)$ of the alkenyl $C-Cl$-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is $-0.72457\,eV$ for the Cl vinyl single bond to $-C(H)=C\ \ C-Cl$ group and $-0.92918\,eV$ for the Cl vinyl single bond to $-C(C)=C\ \ C-Cl$ group. It is based on the energy match between the Cl atom and the $C2sp^3$ HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.54 corresponding to functional-group composition of the molecule.

The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.56.

Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

Functional Group	Group Symbol
Cl vinyl single bond to -C(H)=C	$C-Cl$ (i)
Cl vinyl single bond to -C(C)=C	$C-Cl$ (ii)
CC double bond	$C=C$
C vinyl single bond to -C(C)=C	$C-C$ (i)
C vinyl single bond to -C(H)=C	$C-C$ (ii)
C vinyl single bond to -C(C))=CH_2	$C-C$ (iii)
CH (alkenyl halide)	$C-H$ (i)
CH_2 alkenyl group	$C-H\left(CH_2\right)$ (i)
CH_3 group	$C-H\left(CH_3\right)$
CH_2 alkyl group	$C-H\left(CH_2\right)$ (ii)
CH (alkyl)	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.52. The geometrical bond parameters of branched-chain alkenyl chlorides and experimental values [1].

Parameter	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C=C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-C$ (iii) Group	$C-H\ (CH_2)$ (i) Group	$C-H$ (i) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ (ii) Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_n)$	2.15818	2.19358	1.47228	2.04740	2.04740	2.04740	1.64010	1.60061	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_n)$	1.62912	1.64243	1.26661	1.43087	1.43087	1.43087	1.04566	1.03299	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (A)$	1.72419	1.73827	1.34052	1.51437	1.51437	1.51437	1.10668	1.09327	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.730 (vinyl chloride) 1.73 (1,1-dichloroethylene)	1.730 (vinyl chloride) 1.73 (1,1-dichloroethylene)	1.342 (2-methylpropene) 1.346 (2-butene) 1.349 (1,3-butadiene)		1.508 (2-butene)	1.508 (2-methylpropene)	1.10 (2-methylpropene) 1.108 (avg.) (1,3-butadiene)	1.09 (vinyl chloride)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c\ (a_n)$	1.41552	1.45403	0.75055	1.46439	1.46439	1.46439	1.26354	1.22265	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.75486	0.74874	0.86030	0.69887	0.69887	0.69887	0.63756	0.64537	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.53. The MO to HO intercept geometrical bond parameters of branched-chain alkenyl chlorides. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3 AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{initial}$ (a_o)	r_{final} (a_o)	$E_{Coulomb}(C'2sp^3)$ (eV) Final	$E(C'2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_o)	d_2 (a_o)
$C_b=C'_a(Cl)-H\ (C'H)$ (i)	C'_a	-1.34946	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	76.99	103.01	40.53	1.21653	0.18354
$-C_b=C'_a(H)Cl$ $(C'_a-Cl$ (i))	C'_a	-1.13379	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	79.43	100.57	34.49	1.77872	0.14960
$-C_b=C'_a(H)Cl$ $(C'_a-Cl$ (i))	Cl	-0.72457	0	0	0		1.05158	0.87495	-15.55033		85.36	94.64	38.03	1.69995	0.07083
$-C_b=C'_a(C')Cl$ $(C'_a-Cl$ (ii))	C'_a	1.13379	-0.46459	-0.92918	0	-154.14326	0.91771	0.78405	-17.35332	-17.16245	72.17	107.83	30.88	1.88253	0.24010
$-C_b=C'_a(C')Cl$ $(C'_a-Cl$ (ii))	Cl	-0.46459	0	0	0		1.05158	0.88983	-15.29034		83.62	96.38	37.46	1.74125	0.09882
$C'_a(H)C'_a=C'_aH,C'_a$	C'_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0.49168
$C'_a(H)C'_a=C'_bH_2$	C'_b	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	129.84	50.16	60.70	0.72040	0.54620
$C'_a(C'_d)C'_a=C'_bH,C'_a$	C'_a	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	126.39	53.61	56.95	0.80289	0.46371
$R_1C'_bH_2-C'_a(C')=C'$ $(C'-C'$ (i))	C'_a	-1.13380	-0.72457	-0.72457	0	-154.19863	0.91771	0.78155	-17.40869	-17.21783	60.88	119.12	27.79	1.81127	0.38039
$R_1C'_bH_2-C'_a(C')=C'$ $(C'-C'$ (i)) $R_1C'_bH_2-C'_a(C')=C'H_2$ $(C'-C'$ (iii))	C'_b	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	67.40	112.60	31.36	1.74821	0.31734
$R_1C'_bH_2-C'_a(H)=C'$ $(C'-C'$ (ii))	C'_a	-1.13380	-0.92918	0	0	-153.67866	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$R_1C'_bH_2-C'_a(H)=C'$ $(C'-C'$ (i))	C'_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H\ (C'H_2)$ (i)	C'	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	77.15	102.85	41.13	1.23531	0.18965
$C'-H\ (C'H_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ (C'H_2)$ (ii)	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (C'H)$ (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_2C'_aC'_bH_2C'H_2-$ $(C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_2C'_aC'_bH_2C'H_2-$ $(C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ $(C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$iso(C'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tert(C'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ $(C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tert(C'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$iso(C'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.54. The energy parameters (eV) of functional groups of branched-chain alkenyl chlorides.

Parameters	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C=C$ Group	$C-C$ (i) Group	$C-C$ (ii) Group	$C-C$ (iii) Group	CH_2 (i) Group	$C-H$ (i) Group	CH_3 Group	CH_2 (ii) Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	2	1	1	1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	1	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.81317	0.81317	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	0	1	0	1	1	1	0	1	1	0	0	0	1	1	0
c_4	2	2	4	2	2	2	1	1	1	1	1	2	2	2	2	2	2
c_5	0	0	0	0	0	0	2	1	3	2	1	0	0	0	0	0	0
C_{1v}	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2v}	0.81317	0.81317	0.91771	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_c (eV)	-32.87721	-32.14474	-102.08992	-30.19634	-30.19634	-30.19634	-72.03287	-37.10024	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	8.35160	8.28394	21.48386	9.50874	9.50874	9.50874	26.02344	13.17125	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.61688	7.32700	34.67062	7.37432	7.37432	7.37432	21.95990	11.58941	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-3.80844	-3.66350	-17.33531	-3.68716	-3.68716	-3.68716	-10.97995	-5.79470	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(sp\ ini)$ (eV)	-14.63489	-14.63489	0	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{sp^3 \to sp}(sp\ ini)$ (eV)	-3.71674	-3.19677	0	0	0	0	0	-1.13379	0	0	0	0	0	0	0	0	0
$E_T(sp\ ini)$ (eV)	-10.91815	-10.97139	0	-14.63489	-14.63489	-14.63489	-14.63489	-13.50110	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(sp_2 ini)$ (eV)	-31.63531	-31.63541	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-31.63539	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,sp^3,AO\right)$ (eV)	-1.44915	-0.92918	-2.26759	-1.44915	-1.85836	-1.44915	0	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(sp)$ (eV)	-33.08452	-32.56455	-65.53833	-33.08452	-33.49373	-33.08452	-49.66493	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{14}\ rad/s\right)$	8.31434	8.11389	43.0680	9.97851	16.4962	9.97851	25.2077	26.4826	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	5.47264	5.34070	28.34813	6.56803	10.85807	6.56803	16.59214	17.43132	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D$ (eV)	-0.15312	-0.14888	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.26130	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Keesom}$ (eV)	0.08059 [12]	0.08059 [12]	0.17897 [6]	0.15895 [7]	0.09931 [8]	0.09931 [8]	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{vac}$ (eV)	-0.11282	-0.10859	-0.25568	-0.08827	-0.16869	-0.11809	-0.07727	-0.08364	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{ang} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E_p (Group) (eV)	-33.19734	-32.67314	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-31.71901	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{conj}(e_1, sp\ ini)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{conj}(e_2, sp\ ini)$ (eV)	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
E_D (Group) (eV)	3.77953	3.40336	7.51014	3.75498	4.39264	3.78480	7.83968	3.33765	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.55. The total bond energies of branched-chain alkenyl chlorides calculated using the functional group composition and the energies of Table 15.54 compared to the experimental values [2].

Formula	Name	$C-Cl$ (i)	$C-Cl$ (ii)	$C=C$	$C-C$ (i)	$C-C$ (ii)	$C-C$ (iii)	CH_2 (i)	CH (i)	CH_3	CH_2 (ii)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3Cl	Chloroethene	1	0	1	0	0	0	1	1	0	0	0	0	0	0	0	0	0	22.46700	22.505	0.00170
C_3H_5Cl	2-Chloropropene	0	1	1	0	0	1	1	0	1	0	0	0	0	0	0	0	0	35.02984	35.05482	0.00071

Table 15.56. The bond angle parameters of branched-chain alkenyl chlorides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_1)	$2c'$ Bond 2 (a_2)	$2c'$ Terminal Atoms (a_m)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aCl$ (C_a-Cl (i))	2.06598	3.25825	4.5809	-16.27490 C_a	15	-12.96764 Cl	Cl	0.83600	0.91771	0.75	0.95310 (Eq. (15.65))	0.75	1.09775	0				116.94	
$\angle C_bC_aH$ (C_a-Cl (i))																116.94		121.53	124 (vinyl chloride)
$\angle C_bC_aCl$ (C_a-Cl (i))																116.94		121.53	122.5 (vinyl chloride) 123.8 (1,1-dichloroethylene)
$\angle C_bC_aCl$ (C_a-Cl (i))	2.53321	3.25825	5.1060	-15.75493 C_b	7	-12.96764 Cl	Cl	0.86359	0.86359	1	0.81317 (Eq. (15.111))	1	0.86359	-0.92918				123.19	123.8 (1,1-dichloroethylene) 122.5 (vinyl chloride)
$\angle HC_aC_b$ $\left(C_c(H)C_a=C_b\right)$	2.11323	2.86175	4.2895	-15.95954 C_a	9	-14.82575 C_c	I	0.85252	0.91771	0.75	1	0.75	1.07647	0				118.36	
$\angle C_cC_aC_b$ $\left(C_c(C_c)C_a=C_b\right)$	2.86175	2.86175	4.7958	-16.68411 C_c	24	-16.68411 C_c	24	0.81549	0.81549	1	1	1	0.81549	-1.85836				113.84	
$\angle C_bC_aC_c$ $\left(C_b=C_aC_c\right)$	2.53321	2.86175	4.7559	-16.98873 C_b		-16.68411 C_c	24	0.80361	0.81549	1	1	1	0.81055	-1.85836				123.46	124.4 (1,3,5-hexatriene CbCcCc) 121.7 (1,3,5-hexatriene CaCbCc) 124.4 (1,3-butadiene CCC) 125.3 (2-butene CbCaCc)
$\angle HC_aC_b$																118.36	123.46	118.19	
$\angle HC_aH$ $\left(H_2C_a=C_bC_c\right)$	2.04578	2.04578	3.4756	-15.95955	9	H	H	0.85252	1	1	1	0.75	1.17300	0				116.31	118.5 (2-methylpropene)
$\angle C_bC_aH$ $\left(H_2C_a=C_bC_c\right)$																116.31		121.85	121 (2-methylpropene)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_{ar}	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_{ar}	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_{ar}	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_{ar}	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALCOHOLS ($C_nH_{2n+2}O_m$, $n=1,2,3,4,5...\infty$)

The alkyl alcohols, $C_nH_{2n+2}O_m$, comprise an OH functional group and two types of $C-O$ functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The OH functional group was solved in the Hydroxyl Radical (OH) section. Each $C-O$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the O AO has an energy of $E\left(O\right)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C-O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO\ to\ O\right)=\frac{E(O)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-13.61806\ eV}{-14.63489\ eV}(0.91771)=0.85395 \quad (15.114)$$

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.65376\ eV$ for the CH_3-OH $C-O$ group. It is based on the energy match between the OH group and the $C2sp^3$ HO of a methyl group and is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-0.72457\ eV$ (Eq. (14.151)), respectively. For the alkyl $C-O$ group, $E_T\left(atom-atom,msp^3.AO\right)$ is $-1.85836\ eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group where both energy contributions are given by Eq. (14.513).

The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.57. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 15.61 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.79-15.108) are given in Table 15.62.

Table 15.57. The symbols of functional groups of alkyl alcohols.

Functional Group	Group Symbol
OH group	OH
CH_3OH C-O	$C-O$ (i)
Alkyl C-O	$C-O$ (ii)
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.58. The geometrical bond parameters of alkyl alcohols and experimental values [1].

Parameter	OH Group	$C-O$ (i) Group	$C-O$ (ii) Group	$C-H\left(CH_3\right)$ Group	$C-H\left(CH_2\right)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\left(a_0\right)$	1.26430	1.79473	1.78255	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\left(a_0\right)$	0.91808	1.33968	1.33512	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\left(\AA\right)$	0.971651	1.41785	1.41303	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $\left(\AA\right)$	0.971 (ethanol) 0.9451 (methanol)	1.4246 (methanol)	1.431 (ethanol)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\left(a_0\right)$	0.86925	1.19429	1.18107	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.72615	0.74645	0.74900	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.59. The MO to HO intercept geometrical bond parameters of alkyl alcohols. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Conduction}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
H_3CO-H	O	-0.82688	0	0	0		1.00000	0.86923	-15.65263		115.49	64.51	64.51	0.54405	0.37403
$-H_2C_aO-H$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		115.09	64.91	64.12	0.55182	0.36625
H_3C-OH $(C-O$ (i))	C	-0.82688	0	0	0	-152.44257	0.91771	0.86923	-15.65263	-15.46177	96.59	83.41	46.30	1.23986	0.09981
H_3C-OH $(C-O$ (i))	O	-0.82688	0	0	0		1.00000	0.86923	-15.65263		96.59	83.41	46.30	1.23986	0.09981
$-H_2C_a-OH$ $(C-O$ (ii))	C_a	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	93.09	86.91	43.59	1.29114	0.04398
$-H_2C_a-OH$ $(C-O$ (ii))	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		97.20	82.80	46.50	1.22692	0.10820
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.60. The energy parameters (eV) of functional groups of alkyl alcohols.

Parameters	OH Group	$C-O$ (i) Group	$C-O$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	0.75	1	1	1	1	1	1	1	1	1	1	1
c_2	1	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	2	1	1	1	2	2	2	2	2	2
c_5	1	0	0	3	2	1	0	0	0	0	0	0
C_{1a}	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2a}	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-40.92709	-33.47304	-33.78820	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	14.81988	10.15605	10.19068	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	16.18567	9.32537	9.47749	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ss} (eV)	-8.09284	-4.66268	-4.73874	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(xs\ no)$ (eV)	-13.6181	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(xs\ no)$ (eV)	0	-1.65376	-1.85836	0	0	0	0	0	0	0	0	0
$E_T(xs\ no)$ (eV)	-13.6181	-12.98113	-12.77653	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2xs)$ (eV)	-31.63247	-31.63544	-31.63529	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	0	-1.65376	-1.85836	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(xs)$ (eV)	-31.63537	-33.28912	-33.49373	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	44.1776	22.3978	12.2831	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	29.07844	14.74264	8.08494	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D$ (eV)	-0.33749	-0.25287	-0.18841	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kvib}$ (eV)	0.46311 [17-18]	0.12808 [19]	0.13328 [20]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{mc}$ (eV)	-0.10594	-0.18883	-0.12177	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-31.74130	-33.47795	-33.61550	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(e_1\ xs\ no)$ (eV)	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(e_2\ xs\ no)$ (eV)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{ij}(Group)$ (eV)	4.41035	4.20817	4.34572	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.61. The total bond energies of alkyl alcohols calculated using the functional group composition and the energies of Table 15.60 compared to the experimental values [3].

Formula	Name	*OH* Group	*C–O* (i) Group	*C–O* (ii) Group	CH_3	CH_2	*CH*	*C–C* (a)	*C–C* (b)	*C–C* (c)	*C–C* (d)	*C–C* (e)	*C–C* (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4O	Methanol	1	0	1	1	0	0	0	0	0	0	0	0	21.11038	21.131	0.00097
C_2H_6O	Ethanol	1	0	1	1	1	0	1	0	0	0	0	0	33.40563	33.428	0.00066
C_3H_8O	1-Propanol	1	0	1	1	2	0	2	0	0	0	0	0	45.56333	45.584	0.00046
C_3H_8O	2-Propanol	1	0	1	2	0	1	2	0	0	0	0	0	45.72088	45.766	0.00098
$C_4H_{10}O$	1-Butanol	1	0	1	1	3	0	3	0	0	0	0	0	57.72103	57.736	0.00026
$C_4H_{10}O$	2-Butanol	1	0	1	2	1	1	3	0	0	0	0	0	57.87858	57.922	0.00074
$C_4H_{10}O$	2-Methyl-1-propananol	1	0	1	2	1	1	0	3	0	0	0	0	57.79359	57.828	0.00060
$C_4H_{10}O$	2-Methyl-2-propananol	1	0	1	3	0	0	0	0	3	0	0	0	58.15359	58.126	-0.00048
$C_5H_{12}O$	1-Pentanol	1	0	1	1	4	0	4	0	0	0	0	0	69.87873	69.887	0.00011
$C_5H_{12}O$	2-Pentanol	1	0	1	2	2	1	4	0	0	0	0	0	70.03628	70.057	0.00029
$C_5H_{12}O$	3-Pentanol	1	0	1	2	2	1	4	0	0	0	0	0	70.03628	70.097	0.00087
$C_5H_{12}O$	2-Methyl-1-butananol	1	0	1	2	2	1	2	3	0	0	0	0	69.95129	69.957	0.00008
$C_5H_{12}O$	3-Methyl-1-butananol	1	0	1	2	2	1	1	3	0	0	0	0	69.95129	69.950	-0.00002
$C_5H_{12}O$	2-Methyl-2-butananol	1	0	1	3	1	0	1	0	3	0	0	0	70.31129	70.246	-0.00092
$C_5H_{12}O$	3-Methyl-2-butananol	1	0	1	3	0	2	0	3	0	1	0	0	69.96081	70.083	0.00174
$C_6H_{14}O$	1-Hexanol	1	0	1	1	5	0	5	0	0	0	0	0	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	1	0	1	2	3	1	5	0	0	0	0	0	82.19398	82.236	0.00052
$C_7H_{16}O$	1-Heptanol	1	0	1	1	6	0	6	0	0	0	0	0	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	1	0	1	1	7	0	7	0	0	0	0	0	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	1	0	1	2	13	1	4	3	0	0	0	0	106.42439	106.459	0.00032
$C_9H_{20}O$	1-Nonanol	1	0	1	1	8	0	8	0	0	0	0	0	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	1	0	1	1	9	0	9	0	0	0	0	0	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	1	0	1	1	11	0	11	0	0	0	0	0	154.98263	154.984	0.00001
$C_{16}H_{34}O$	1-Hexadecanol	1	0	1	1	15	0	15	0	0	0	0	0	203.61343	203.603	-0.00005

Table 15.62. The bond angle parameters of alkyl alcohols and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_a OH$ (C_a-O (i))	2.67935	1.83616	3.6697	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				107.24	108.53 (methanol)
$\angle C_a OH$ (C_a-O (ii))	2.67024	1.83616	3.6515	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				106.78	105 (ethanol)
$\angle C_b C_a O$ (C_a-O (ii))	2.91547	2.67024	4.5826	-16.68412	25	-13.61806	O	0.81549	0.85395 (Eq (15.114))	1	1	1	0.83472	-1.65376				110.17	107.8 (ethanol)
Methylene $\angle HC_a H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_a C_b C_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_a C_b H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_a H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_a C_b C_c$															70.56			109.44	
$\angle C_a C_b H$															70.56			109.44	
$\angle C_b C_a C_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_b C_a H$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_a C_b H$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_b C_a C_c$ ten C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_b C_a C_d$															72.50			107.50	

ETHERS ($C_nH_{2n+2}O_m$, $n=2,3,4,5...\infty$)

The alkyl ethers, $C_nH_{2n+2}O_m$, comprise two types of $C-O$ functional groups, one for methyl or t-butyl groups corresponding to the C and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each $C-O$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of $E\left(C,2sp^3\right)=-14.63489\,eV$ (Eq. (15.25)) and the O AO has an energy of $E\left(O\right)=-13.61806\,eV$. To meet the equipotential condition of the union of the $C-O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eq. (15.113) is $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.44915\,eV$ for the CH_3-O- and $\left(CH_3\right)_3C-O-$ $C-O$ groups. It is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), and the $C2sp^3$ HO of a methyl group as given by Eq. (14.151). For the alkyl $C-O$ group, $E_T\left(atom-atom,msp^3.AO\right)$ is $-1.65376\,eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group and is given by the linear combination of $-0.72457\,eV$ (Eq. (14.151)) and $-0.92918\,eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.79-15.108) are given in Table 15.68.

Table 15.63. The symbols of functional groups of alkyl ethers.

Functional Group	Group Symbol
C-O (CH_3-O- and $(CH_3)_3C-O-$)	$C-O$ (i)
C-O (alkyl)	$C-O$ (ii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.64. The geometrical bond parameters of alkyl ethers and experimental values [1].

Parameter	$C-O$ (i) Group	$C-O$ (ii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.80717	1.79473	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.34431	1.33968	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.42276	1.41785	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.416 (dimethyl ether)	1.418 (ethyl methyl ether (avg.))	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.20776	1.19429	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.74388	0.74645	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.65. The MO to HO intercept geometrical bond parameters of alkyl ethers. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ \left(OC_aH_3\right)$	C_a	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	78.85	101.15	42.40	1.21777	0.16921
$H_3C_a-O-C_aH_3$ $(CH_3)_3C_a-O-C_bH_3$ $(CH_3)_3C_a-O-C_a(CH_3)_3$ $(C-O$ (i))	$C_{a\,b}$	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$H_3C_a-O-C_aH_3$ $(CH_3)_3C_a-O-C_bH_3$ $(CH_3)_3C_a-O-C_a(CH_3)_3$ $(C-O$ (i))	O	-0.72457	-0.72457	0	0		1.00000	0.83600	-16.27490		92.66	87.34	43.74	1.30555	0.03876
$-H_2C_a-OC_b(CH_3)_3$ $-H_2C_a-OC_bH_3$ $(C-O$ (ii))	C_a	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.58181	-16.39095	92.41	87.59	43.35	1.30512	0.03456
$-H_2C_a-OC_b(CH_3)_3$ $-H_2C_a-OC_bH_3$ $(C-O$ (ii))	O	-0.72457	-0.82688	0	0		1.00000	0.83078	-16.37720		93.33	86.67	43.98	1.29138	0.04829
$-H_2C_a-O-H_2C_a-$ $(C-O$ (ii))	O	-0.82688	-0.82688	0	0		1.00000	0.82562	-16.47951		92.87	87.13	43.66	1.29829	0.04138
$C-H\ \left(CH_3\right)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ \left(CH_2\right)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ \left(CH\right)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$IsoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.66. The energy parameters (eV) of functional groups of alkyl ethers.

Parameters	$C-O$ (i) Group	$C-O$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1v}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2v}	1	1	1	1	1	1	1	1	1	1	1
V_c (eV)	-33.15757	-33.47304	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	10.12103	10.15605	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	9.17389	9.32537	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-4.58695	-4.66268	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\text{no no})$ (eV)	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{\pi_2 NO}(\text{no no})$ (eV)	-1.44915	-1.65376	0	0	0	0	0	0	0	0	0
$E_T(\text{no no})$ (eV)	-13.18574	-12.98113	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(\pi_2 NO)$ (eV)	-31.63533	-31.63544	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, nsp^3.AO\right)$ (eV)	-1.44915	-1.65376	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(NO)$ (eV)	-33.08452	-33.28912	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	12.0329	12.1583	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_g (eV)	7.92028	8.00277	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_p$ (eV)	-0.18420	-0.18631	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kvib}$ (eV)	0.13663 [21]	0.16118 [4]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{vib}$ (eV)	-0.11589	-0.10572	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{nbng} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-33.20040	-33.39484	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(\varepsilon, \text{no no})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(\varepsilon, \text{no no})$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_p(Group)$ (eV)	3.93062	4.12506	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.67. The total bond energies of alkyl ethers calculated using the functional group composition and the energies of Table 15.66 compared to the experimental values [3].

Formula	Name	C–O (i) Group	C–O (ii) Group	CH_3	CH_2	CH	C–C (a)	C–C (b)	C–C (c)	C–C (d)	C–C (e)	C–C (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6O	Dimethyl ether	2	0	2	0	0	0	0	0	0	0	0	32.84496	32.902	0.00174
C_3H_8O	Ethyl methyl ether	1	1	2	1	0	1	0	0	0	0	0	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	0	2	2	2	0	2	0	0	0	0	0	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	1	1	2	2	0	2	0	0	0	0	0	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	1	1	3	0	1	0	2	0	0	0	0	57.45569	57.499	0.00075
$C_6H_{14}O$	Dipropyl ether	0	2	2	4	0	4	0	0	0	0	0	81.86464	81.817	-0.00059
$C_6H_{14}O$	Diisopropyl ether	0	2	4	0	2	0	4	0	0	0	0	82.06642	82.088	0.00026
$C_6H_{14}O$	t-Butyl ethyl ether	1	1	4	1	0	1	0	3	0	0	0	82.10276	82.033	-0.00085
$C_7H_{16}O$	t-Butyl isopropyl ether	1	1	5	0	1	0	2	3	0	0	0	94.36135	94.438	0.00081
$C_8H_{18}O$	Dibutyl ether	0	2	2	6	0	6	0	0	0	0	0	106.18004	106.122	-0.00055
$C_8H_{18}O$	Di-sec-butyl ether	0	2	4	2	2	2	4	0	0	0	0	106.38182	106.410	0.00027
$C_8H_{18}O$	Di-t-butyl ether	2	0	6	0	0	0	0	6	0	0	0	106.65628	106.425	-0.00218
$C_8H_{18}O$	t-Butyl isobutyl ether	1	1	5	1	1	0	3	3	0	0	0	106.49072	106.497	0.00006

Table 15.68. The bond angle parameters of alkyl ethers and experimental values [1]. In the calculation of θ_e, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Conbumba}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Conbumba}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_aOC_a$ (C_a-O (i))	2.68862	2.68862	4.4721	-17.40869	38	-17.40869	38	0.78155	0.78155	1	1	1	0.78155	-1.85836				112.54	112 (dimethyl ether)
$\angle C_aOC_b$ (C_a-O (i)) (C_b-O (ii))	2.68862	2.67935	4.4385	-17.51099	41	-17.51099	41	0.77699	0.77699	1	1	1	0.77699	-1.85836				111.55	111.9 (ethyl methyl ether)
$\angle C_bC_aO$ (C_a-O (ii))	2.91547	2.67935	4.5607	-16.68412	25	-13.61806	O	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				109.13	109.4 (ethyl methyl ether)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

PRIMARY AMINES ($C_nH_{2n+2+m}N_m$, $n=1,2,3,4,5...\infty$)

The primary amines, $C_nH_{2n+2+m}N_m$, comprise an NH_2 functional group and a $C-N$ functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino (NH_2) functional group was solved using the procedure given in the Dihydrogen Nitride (NH_2) section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.52) are $n_1=2$, $C_1=0.75$, $C_2=0.93613$ (Eqs. (13.248-13.249)), $C_{1\sigma}=1.5$, and $c_1=0.75$. In primary amines, the $C2sp^3$ HO of the $C-NH_2$-bond MO has an energy of $E\left(C,2sp^3\right)=-15.35946\,eV$ (Eq. (15.18) with $s=1$ and Eqs. (15.19-15.20)) and the N AO has an energy of $E\left(N\right)=-14.53414\,eV$. To meet the equipotential condition of the union of the $N-H$ H_2-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 of Eq. (15.52) for the $N-H$-bond MO given by Eq. (15.68) is

$$c_2\left(H\ to\ 1°N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}=\frac{-14.53414\,eV}{-15.35946\,eV}=0.94627 \tag{15.115}$$

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\,eV$ (Eq. (15.25)), and the N AO has an energy of $E\left(N\right)=-14.53414\,eV$. To meet the equipotential condition of the union of the

$C-N$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-N$-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO\ to\ N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-14.53414\ eV}{-14.63489\ eV}(0.91771)=0.91140 \quad (15.116)$$

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.44915\ eV$. It is based on the energy match between the N of the NH_2 group and the $C2sp^3$. HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)), where the $N-H$ bonds are also energy matched to the $C-N$ bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.79-15.108) are given in Table 15.74.

Table 15.69. The symbols of functional groups of primary amines.

Functional Group	Group Symbol
NH_2 group	NH_2
C-N	$C-N$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.70. The geometrical bond parameters of primary amines and experimental values [1].

Parameter	NH_2 Group	$C-N$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.28083	1.92682	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	0.95506	1.38810	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.0108	1.46910	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.010 (methylamine)	1.471 (methylamine)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.85345	1.33634	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.74566	0.72041	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.71. The MO to HO intercept geometrical bond parameters of primary amines. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$H_3CN(H)-H$	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		118.00	62.00	64.85	0.54432	0.41075
$-H_2C_aN(H)-H$	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		118.00	62.00	64.85	0.54432	0.41075
H_3C-NH_2	C	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	85.28	94.72	40.73	1.46010	0.07200
H_3C-NH_2	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		85.28	94.72	40.73	1.46010	0.07200
$-H_2C_a-NH_2$	C_a	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	80.20	99.80	37.50	1.52858	0.14048
$-H_2C_a-NH_2$	N	-0.72457	0	0	0		0.93084	0.87495	-15.55033		85.28	94.72	40.73	1.46010	0.07200
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C'$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.72. The energy parameters (eV) of functional groups of primary amines.

Parameters	NH_2 Group	$C-N$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	1	0	0	0	0	0	0	0	0	0	0
c_1	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
c_2	0.93613	1	1	1	1	1	1	1	1	1	1
c_1	0.75	1	1	1	1	1	1	1	1	1	1
c_2	0.94627	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	1	1	1	2	2	2	2	2	2
c_5	2	0	3	2	1	0	0	0	0	0	0
c_{1n}	1.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
c_{2n}	1	1	1	1	1	1	1	1	1	1	1
V_c (eV)	-77.89897	-32.46339	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	28.49191	9.80175	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	30.40957	8.42409	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-15.20478	-4.21204	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(sp^3\ HO)$ (eV)	-14.53414	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(sp^3\ HO)$ (eV)	0	-1.44915	0	0	0	0	0	0	0	0	0
$E_T(sp^3\ HO)$ (eV)	-14.53414	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E(s,sp^3\ HO)$ (eV)	-14.53414	0	0	0	0	0	0	0	0	0	0
$E_T(H_2MO)$ (eV)	-48.73642	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom,msp^3,AO)$ (eV)	0	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-48.73660	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	64.2189	18.9231	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	42.27003	12.45552	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
E_D (eV)	-0.40690	-0.23100	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
E_{Kwk} (eV)	0.40929 [22]	0.12944 [23]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
E_{anc} (eV)	-0.20226	-0.16628	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-49.14112	-33.25079	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{mutual}(s,sp\ HO)$ (eV)	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{mutual}(s,sp\ HO)$ (eV)	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	7.41010	3.98101	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.73. The total bond energies of primary amines calculated using the functional group composition and the energies of Table 15.72 compared to the experimental values [3].

Formula	Name	NH_2 Group	$C-N$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_5N	Methylamine	1	1	1	0	0	0	0	0	0	0	0	23.88297	23.857	-0.00110
C_2H_7N	Ethylamine	1	1	1	1	0	1	0	0	0	0	0	36.04067	36.062	0.00060
C_3H_9N	Propylamine	1	1	1	2	0	2	0	0	0	0	0	48.19837	48.243	0.00092
$C_4H_{11}N$	Butylamine	1	1	1	3	0	3	0	0	0	0	0	60.35607	60.415	0.00098
$C_4H_{11}N$	sec-Butylamine	1	1	2	1	1	1	2	0	0	0	0	60.45696	60.547	0.00148
$C_4H_{11}N$	t-Butylamine	1	1	3	0	0	0	0	3	0	0	0	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	1	1	2	1	1	0	3	0	0	0	0	60.42863	60.486	0.00094

Table 15.74. The bond angle parameters of primary amines and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_T (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HNH$	1.91013	1.91013	3.0984	-14.53414	N	H	H	0.94627 Eq. (15.115))	1	1	1	0.75	1.05679	0				108.40	107.1 (methylamine)
$\angle HNC_a$	1.91013	2.77620	3.8816	-14.53414	5	-15.35946	N	0.91140 (Eq. (15.116))	0.88583	0.75	1	0.75	0.97194	0				110.48	110.3 (methylamine)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	108.0 (methylamine) 107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

SECONDARY AMINES ($C_nH_{2n+2+m}N_m$, $n=2,3,4,5...\infty$)

The secondary amines, $C_nH_{2n+2+m}N_m$, comprise an NH functional group and two types of $C-N$ functional groups, one for the methyl group corresponding to the C of $C-N$ and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino (NH) functional group was solved using the procedure given in the Hydrogen Nitride (NH) section. Using the results of Eqs. (13.245-13.316), the secondary amino parameters in Eq. (15.52) are $n_1=1$, $C_1=0.75$, $C_2=0.93613$ (Eqs. (13.248-13.249)), $C_{1o}=0.75$, and $c_1=0.75$. In secondary amines, the $C2sp^3$ HO of the $C-NH$-bond MO has an energy of $E\left(C,2sp^3\right)=-15.56407\,eV$ (Eqs. (14.514-14.516)); Eq. (15.29) with $s=1$ and $s=2$, Eq. (15.31), and Eqs. (15.19-15.20)) and the N AO has an energy of $E\left(N\right)=-14.53414\,eV$. To meet the equipotential condition of the union of the $N-H$ H_2-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 of Eq. (15.52) for the $N-H$-bond MO given by Eq. (15.68) is

$$c_2\left(H\ to\ 2°N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}=\frac{-14.53414\,eV}{-15.56407\,eV}=0.93383 \tag{15.117}$$

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\,eV$ (Eq. (15.25)), and the N AO has an energy of $E\left(N\right)=-14.53414\,eV$. To meet the equipotential condition of the union of the

$C-N$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-N$-bond MO given by Eq. (15.116) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$.

As given in the Continuous-Chain Alkanes (C_nH_{2n+2}, $n=3,4,5...\infty$) section, each methylene group forms two single bonds, and the energy of each $C2sp^3$ HO of each CH_2 group alone is given by that in ethylene, $-1.13379\ eV$ (Eq. (14.511)). In secondary amines, the N of the NH group also binds to two $C2sp^3$ HOs and the corresponding $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379\ eV$. It is based on the energy match between the N of the NH group to the two $C2sp^3$ HOs corresponding to the energy contributions to each of the two single bonds that are equivalent to those of independent methylene groups, $-1.13379\ eV$ (Eq. (14.511)), where the $N-H$ bond is also energy matched to the $C-N$ bonds. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379\ eV$. It is based on the energy match between the N of the NH group to two $C2sp^3$ HOs corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, $-0.72457\ eV$ (Eq. (14.151)), where the $N-H$ bonds are also energy matched to the $C-N$ bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of secondary amines are given in Tables 15.76, 15.77, and 15.78, respectively. As in the case of NH_2 (Eq. (13.339)), $C_{1o}=2C_1$ rather than $C_{1o}=C_1$ in Eq. (15.52) for the $C-N$ bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.79-15.108) are given in Table 15.80.

Table 15.75. The symbols of functional groups of secondary amines.

Functional Group	Group Symbol
NH group	NH
C-N (methyl)	$C-N$ (i)
C-N (alkyl)	$C-N$ (ii)
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.76. The geometrical bond parameters of secondary amines and experimental values [1].

Parameter	NH Group	$C-N$ (i) Group	$C-N$ (ii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.26224	1.94862	1.94862	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	0.94811	1.39593	1.39593	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.00343	1.47739	1.47739	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.00 (dimethylamine)	1.455 (dimethylamine)		1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,c\ (a_0)$	0.83327	1.35960	1.35960	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.75113	0.71637	0.71637	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.77. The MO to HO intercept geometrical bond parameters of secondary amines. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$H_3C_aN(C_bH_3)-H$	N	-0.56690	-0.56690	0	0		0.93084	0.85252	-15.95954		118.18	61.82	64.40	0.54546	0.40264
$-H_2C_aN(R_{attyl})-H$	N	-0.56690	-0.56690	0	0		0.93084	0.85252	-15.95954		118.18	61.82	64.40	0.54546	0.40264
$H_3C_a-NH-C_aH_3$	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	84.14	95.86	40.30	1.48625	0.09032
$H_3C_a-NH-C_aH_3$	N	-0.56690	-0.56690	0	0		0.93084	0.85252	-15.95954		80.95	99.05	38.26	1.53008	0.13415
$-H_2C_a-NH-C_bR$	C_a	-0.56690	-0.92918	0	0	-153.11177	0.91771	0.83360	-16.32183	-16.13097	78.89	101.11	36.99	1.55650	0.16057
$-H_2C_a-NH-C_bH_2-$	N	-0.56690	-0.56690	0	0		0.93084	0.85252	-15.95954		80.95	99.05	38.26	1.53008	0.13415
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.78. The energy parameters (eV) of functional groups of secondary amines.

Parameters	NH Group	$C-N$ (i) Group	$C-N$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.93613	1	1	1	1	1	1	1	1	1	1	1
c_1	0.75	1	1	1	1	1	1	1	1	1	1	1
c_2	0.93383	0.91140	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	2	1	1	1	2	2	2	2	2	2
c_5	1	0	0	3	2	1	0	0	0	0	0	0
C_{1v}	0.75	1	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2v}	1	1	1	1	1	1	1	1	1	1	1	1
$V_e\ (eV)$	-39.21967	-31.98456	-31.98456	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_\rho\ (eV)$	14.35050	9.74677	9.74677	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	15.53581	8.20698	8.20698	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_{ii}\ (eV)$	-7.76790	-4.10349	-4.10349	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(xo\ no)\ (eV)$	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(xo\ no)\ (eV)$	0	-1.13379	-1.13379	0	0	0	0	0	0	0	0	0
$E_T(xo\ no)\ (eV)$	-14.53414	-13.50110	-13.50110	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)\ (eV)$	-31.63541	-31.63540	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3,A()\right)\ (eV)$	0	-1.13379	-1.13379	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)\ (eV)$	-31.63537	-32.76916	-32.76916	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	47.0696	15.1983	26.0778	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	30.98202	10.00377	17.16484	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D\ (eV)$	-0.34836	-0.20505	-0.26859	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kmb}\ (eV)$	0.40696 [24]	0.12944 [23]	0.11159 [25]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{ave}\ (eV)$	-0.14488	-0.14033	-0.21280	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(group)\ (eV)$	-31.78025	-32.90949	-32.98196	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(e_1\ no\ no)\ (eV)$	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(e_2\ no\ no)\ (eV)$	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)\ (eV)$	3.50582	3.63971	3.71218	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.79. The total bond energies of secondary amines calculated using the functional group composition and the energies of Table 15.78 compared to the experimental values [3].

Formula	Name	NH Group	$C-N$ (i) Group	$C-N$ (ii) Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_7N	Dimethylamine	1	2	0	2	0	0	0	0	0	0	0	0	35.76895	35.765	-0.00012
$C_4H_{11}N$	Diethylamine	1	0	2	2	2	0	2	0	0	0	0	0	60.22930	60.211	-0.00030
$C_6H_{15}N$	Dipropylamine	1	0	2	2	4	0	4	0	0	0	0	0	84.54470	84.558	0.00016
$C_6H_{15}N$	Diisopropylamine	1	0	2	4	0	2	0	4	0	0	0	0	84.74648	84.846	0.00117
$C_8H_{19}N$	Dibutylamine	1	0	2	2	6	0	6	0	0	0	0	0	108.86010	108.872	0.00011
$C_8H_{19}N$	Diisobutylamine	1	0	2	4	2	2	0	6	0	0	0	0	109.00522	109.106	0.00092

Table 15.80. The bond angle parameters of secondary amines and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HCN$ ($C-N$ (i) & (ii))	2.09711	2.79186	4.0661	-14.82575	N	-14.53414	I	0.91771	0.93383 Eq. (15.117))	0.75	I	0.75	1.01756	0				111.76	112 (dimethylamine)
$\angle HNC_a$ ($C-N$ (i) & (ii))	1.89621	2.79186	3.8123	-14.53414	7	-15.56407 (Eq. (15.117))	N	0.91140 (Eq. (15.116))	0.87418	0.75	I	0.75	0.95917	0				107.27	107 (dimethylamine)
$\angle CNC$ ($C-N$ (i) & (ii))	2.79186	2.79186	4.6260	-17.04640	29	-17.04640	29	0.79816	0.79816	I	I	I	0.79816	-1.85836				111.89	111.8 (dimethylamine)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	I	I	I	0.75	1.15796	0				108.44	107 (dimethylamine) 107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	I	I	I	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	I	I	I	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	I	0.87495	0.91771	0.75	I	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	I	0.87495	0.91771	0.75	I	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	I	0.87495	0.91771	0.75	I	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

TERTIARY AMINES ($C_nH_{2n+3}N$, $n=3,4,5...\infty$)

The tertiary amines, $C_nH_{2n+3}N$, have three $C-N$ bonds to methyl or alkyl groups wherein $C-N$ comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In tertiary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\,eV$ (Eq. (15.25)), and the N AO has an energy of $E\left(N\right)=-14.53414\,eV$. To meet the equipotential condition of the union of the $C-N$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-N$-bond MO given by Eq. (15.116) is $c_2\left(C2sp^3HO\ to\ \mathrm{N}\right)=0.91140$.

As given in the Continuous-Chain Alkanes (C_nH_{2n+2}, $n=3,4,5...\infty$) section, the energy of each $C2sp^3$ HO must be a linear combination of that of the CH_3 and CH_2 groups that serve as basis elements. Each CH_3 forms one $C-C$ bond, and each CH_2 group forms two. Thus, the energy of each $C2sp^3$ HO of each CH_3 and CH_2 group alone is given by that in ethane, $-0.72457\,eV$ (Eq. (14.151)), and ethylene, $-1.13379\,eV$ (Eq. (14.511)), respectively. In order to match the energy of the component HOs and MOs for the entire molecule, the energy $E_{T_{alkane}}\left(C-C,2sp^3\right)$ given as a linear combination of these basis elements is $-0.92918\,eV$ (Eq. (14.513)). In tertiary amines, the N binds to three $C2sp^3$ HOs and the corresponding $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-N$-bond MO in Eq. (15.52) due to the charge donation

from the C and N atoms to the MO is $-0.92918\ eV$. It comprises a linear combination of the energy for a primary amine, $-0.72457\ eV$ and a secondary amine, $-1.13379\ eV$.

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.79-15.108) are given in Table 15.86.

Table 15.81. The symbols of functional groups of tertiary amines.

Functional Group	Group Symbol
C-N	$C-N$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.82. The geometrical bond parameters of tertiary amines and experimental values [1].

Parameter	$C-N$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.96313	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.40112	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (A)$	1.48288	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.458 (trimethylamine)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.37505	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.71372	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.83. The MO to HO intercept geometrical bond parameters of tertiary amines. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$N-\left(C_aH_3\right)_3$	C_a	-0.46459		0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	83.37	96.63	40.00	1.50383	0.10271
$N-\left(C_aH_3\right)_3$	N	-0.46459	-0.46459	-0.46459	0		0.93084	0.83885	-16.21953		78.02	101.98	36.64	1.57525	0.17413
$N-\left(C_aH_2-\right)_3$	C_a	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21953	-16.02866	78.02	101.98	36.64	1.57525	0.17413
$N-\left(C_aH_2-\right)_3$	N	-0.46459	-0.46459	-0.46459	0		0.93084	0.83885	-16.21953		78.02	101.98	36.64	1.57525	0.17413
$C-H\left(CH_3\right)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_2\right)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\left(CH\right)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0 72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.84. The energy parameters (eV) of functional groups of tertiary amines.

Parameters	$C-N$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	3	2	1	1	1	1	1	1	1
n_2	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1
c_2	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	1	1	0	0	0	1	1	0
c_4	2	1	1	1	2	2	2	2	2	2
c_5	0	3	2	1	0	0	0	0	0	0
C_{1a}	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2a}	1	1	1	1	1	1	1	1	1	1
V_c (eV)	-31.67393	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	9.71067	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	8.06719	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-4.03359	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(xo\ no)$ (eV)	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(xo\ no)$ (eV)	-0.92918	0	0	0	0	0	0	0	0	0
$E_T(xo\ no)$ (eV)	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	18.1298	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	11.93333	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.22255	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kmb}$ (eV)	0.12944 [23]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{ene}$ (eV)	-0.15783	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-32.72238	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(e,xo\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(e,xo\ no)$ (eV)	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.45260	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.85. The total bond energies of tertiary amines calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

Formula	Name	$C-N$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_9N	Trimethylamine	3	3	0	0	0	0	0	0	0	0	47.83338	47.761	-0.00152
$C_6H_{15}N$	Triethylamine	3	3	3	0	3	0	0	0	0	0	84.30648	84.316	0.00012
$C_9H_{21}N$	Tripropylamine	3	3	6	0	6	0	0	0	0	0	120.77958	120.864	0.00070

Table 15.86. The bond angle parameters of tertiary amines and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	$\bar{c}_1$	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CNC$	2.80224	2.80224	4.6043	-17.14871	1	-17.14871	6	0.79340	0.79340	1	1	1	0.79340	-1.85836				110.48	110.9 (trimethylamine)
Methylene $\angle HC_uH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (dimethylamine) 107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_uH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALDEHYDES ($C_nH_{2n}O$, $n=1,2,3,4,5...\infty$)

The alkyl aldehydes, $C_nH_{2n}O$, each have a $HC=O$ moiety that comprises a $C=O$ functional group and a CH functional group. The single bond of carbon to the carbonyl carbon atom, $C-C(O)H$, is a functional group. In addition to the $C=O$ functional group, formaldehyde comprises a CH_2 functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that E_{mag} is not subtracted since unpaired electrons are not created with fragmentation of the CH functional group of aldehydes. The CH_2 functional group of formaldehyde is solved in the Dihydrogen Carbide (CH_2) section except that the energy of each $C-H$ MO is matched to the initial energy of the $C2sp^3$ HO (Eq. (15.25)). The $C=O$ and $C-C(O)H$ groups are solved by hybridizing the $2s$ and $2p$ AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the O AO has an energy of $E\left(O\right)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C=O$-bond MO given by Eq. (15.114) is $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$. The unpaired electrons created by bond breakage of the double $C=O$ bond requires that two times

the $O2p$ AO magnetic energy E_{mag} (Eq. (15.60)) be subtracted from the total energy to give $E_D(Group)$ (eV) for $C=O$.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $C=O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-2.69893\ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, $-1.13379\ eV$ (Eq. (14.247)), and a triple bond, $-1.56513\ eV$ (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the $C-H$ bond in addition to the pair involved directly in the double bond with O. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-C(O)H$ group is equivalent to that of an alkane, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the aldehyde. In order to match energy between the groups bonded to the $C=O$, electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing, $C_{1o}=2C_1$ rather than $C_{1o}=C_1$ in Eq. (15.52) for the $C-C(O)H$ bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.79-15.108) are given in Table 15.92.

Table 15.87. The symbols of functional groups of alkyl aldehydes.

Functional Group	Group Symbol
CH_2 (formaldehyde) group	$C-H\ (CH_2)$ (i)
CH (aldehyde) group	CH (i)
C=O	$C=O$ (i)
C-C(O)H	$C-C(O)H$
CH_3 group	$C-H\ (CH_3)$
CH_2 (alkyl) group	$C-H\ (CH_2)$ (ii)
CH (alkyl)	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.88. The geometrical bond parameters of alkyl aldehydes and experimental values [1].

Parameter	$C'-H\ (CH_2)$ (i)	CH (i) Group	$C=O$ Group	$C-C(O)H$ Group	$C'-H\ (CH_3)$ Group	$C-H\ (CH_2)$ (ii) Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.64010	1.67465	1.29907	2.04740	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.04566	1.05661	1.13977	1.43087	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.10668	1.11827	1.20628	1.51437	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.116 (formaldehyde)	1.128 (acetaldehyde)	1.208 (formaldehyde) 1.210 (acetaldehyde)	1.515 (acetaldehyde)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,c\ (a_0)$	1.26354	1.29924	0.62331	1.46439	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.63756	0.63095	0.87737	0.69887	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.89. The MO to HO intercept geometrical bond parameters of alkyl aldehydes. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$HC'(O)-H\ (CH_2)$ (i)	C'	-1.34946	0	0	0	-152.96515	0.91771	0.84115	-16.17521	-15.98435	75.72	104.28	40.18	1.25314	0.20748
$-C_bH_2C_a(O)-H\ (CH)$ (i)	C_a	-1.34946	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	64.95	115.05	33.69	1.39345	0.33684
$H_2C=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$-C_bH_2C_a(H)=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RH_2C_b-C_a(H)(O)$	C_a	-1.34946	-0.92918	0	0	-153.89434	0.91771	0.79546	-17.10440	-16.91353	135.34	44.66	63.78	0.57401	0.56576
$H_2C_b-C_a(H)(O)$	C_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$-C_bH_2-C_a(H)(O)$	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H\ (CH_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ (CH_2)$ (ii)	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (CH)$ (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC_bH_2CH_2-$ $(C'-C'\ (a))$	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'\ (a))$	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C'-C'\ (b))$	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C'-C'\ (c))$	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C'-C'\ (d))$	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C'-C'\ (e))$	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C'-C'\ (f))$	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C'-C'\ (f))$	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.90. The energy parameters (eV) of functional groups of alkyl aldehydes.

Parameters	CH_2 (i)	CH (i) Group	$C=O$ Group	$C-C(O)H$ Group	CH_3 Group	CH_2 (ii) Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	2	1	3	2	1	1	1	1	1	1	1
n_2	1	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	1	0	2	0	0	1	1	0	0	0	1	1	0
c_4	1	1	4	2	1	1	1	2	2	2	2	2	2
c_5	2	1	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	0.75	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1
V_σ (eV)	-72.03287	-35.12015	-111.25473	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_π (eV)	26.02344	12.87680	23.87467	9.50874	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	21.95990	10.48582	42.82081	7.37432	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ni} (eV)	-10.97995	-5.24291	-21.41040	-3.68716	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\sigma\text{-}\sigma)$ (eV)	-14.63489	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(\sigma\text{-}\sigma)$ (eV)	0	0	-2.69893	0	0	0	0	0	0	0	0	0	0
$E_T(\sigma\text{-}\sigma)$ (eV)	-14.63489	-14.63489	2.69893	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(\pi_2\text{-}\pi)$ (eV)	-49.66437	-31.63533	-63.27074	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, msp^3.A()\right)$ (eV)	0	0	-2.69893	-1.85836	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(\pi\sigma)$ (eV)	-49.66493	-31.63537	-65.96966	-33.49373	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	25.2077	24.1759	59.4034	23.3291	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	16.59214	15.91299	39.10034	15.35563	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_{Pi}$ (eV)	-0.25493	-0.24966	-0.40804	-0.25966	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.21077 [12]	0.13800 [26]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.07727	-0.07200	-0.30266	-0.19066	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{ang} (eV)	0.14803	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(group)$ (eV)	-49.81948	-31.70737	-66.57498	-33.68439	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(\sigma_1\text{-}\sigma)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(\sigma_2\text{-}\sigma)$ (eV)	-13.59844	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{Pi}(group)$ (eV)	7.83968	3.47404	7.80660	4.41461	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.91. The total bond energies of alkyl aldehydes calculated using the functional group composition and the energies of Table 15.90 compared to the experimental values [3].

Formula	Name	CH_2 (i) Group	CH (i) Group	$C=O$ Group	$C-C(O)H$ Group	CH_3	CH_2 (ii)	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O	Formaldehyde	1	0	1	0	0	0	0	0	0	0	0	0	0	15.64628	15.655	0.00056
C_2H_4O	Acetaldehyde	0	1	1	1	1	0	0	0	0	0	0	0	0	28.18711	28.198	0.00039
C_3H_6O	Propanal	0	1	1	1	1	1	0	1	0	0	0	0	0	40.34481	40.345	0.00000
C_4H_8O	Butanal	0	1	1	1	1	2	0	2	0	0	0	0	0	52.50251	52.491	-0.00022
C_4H_8O	Isobutanal	0	1	1	1	2	0	1	0	2	0	0	0	0	52.60340	52.604	0.00001
$C_5H_{10}O$	Pentanal	0	1	1	1	1	3	0	3	0	0	0	0	0	64.66021	64.682	0.00034
$C_7H_{14}O$	Heptanal	0	1	1	1	1	5	0	5	0	0	0	0	0	88.97561	88.942	-0.00038
$C_8H_{16}O$	Octanal	0	1	1	1	1	6	0	6	0	0	0	0	0	101.13331	101.179	0.00045
$C_8H_{16}O$	2-Ethylhexanal	0	1	1	1	2	4	1	3	3	0	0	0	0	101.20587	101.259	0.00053

Table 15.92. The bond angle parameters of alkyl aldehydes and experimental values [1]. In the calculation of θ_o, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1'	C_2'	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_a'H$ ($C_aH_2(O)$ (i))	2.09132	2.09132	3.5637	-16.39089	18	H	H	0.83008	1	1	1	0.75	1.20470	0				116.87	116.5 (formaldehyde)
$\angle C_b'C_aH$ $RC_a'(H)=O$	2.86175	2.11323	4.2269	-15.75493 C_a'	7	-14.82575 C_b'	1	0.86359	0.91771	0.75	1	0.75	1.06267	0				115.52	115.3 (acetaldehyde)
$\angle C_b'C_aO$	2.86175	2.27954	4.5826	-16.68412	25	-13.61806	0	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				125.70	124.1 (acetaldehyde)
Methylene $\angle HC_a'H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_a'H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	109.8 (acetaldehyde)
$\angle C_a'C_bC_c$															70.56			109.44	
$\angle C_a'C_bH$															70.56			109.44	
$\angle C_b'C_aC_c$ iso C_a'	2.91547	2.91547	4.7958	-16.68412 C_b'	25	-16.68412 C_c'	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_b'C_aH$ iso C_a'	2.91547	2.11323	4.1633	-15.55033 C_a'	5	-14.82575 C_b'	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_a'C_bH$ iso C_a'	2.91547	2.09711	4.1633	-15.55033 C_b'	5	-14.82575 C_a'	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a'	2.90327	2.90327	4.7958	-15.55033 C_b'	5	-14.82575 C_c'	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

KETONES ($C_nH_{2n}O$, $n=1,2,3,4,5...\infty$)

The alkyl ketones, $C_nH_{2n}O$, each have a $C=O$ moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The $C=O$ and $C-C(O)$ groups are solved by hybridizing the $2s$ and $2p$ AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\,eV$ (Eq. (15.25)) and the O AO has an energy of $E\left(O\right)=-13.61806\,eV$. To meet the equipotential condition of the union of the $C=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C=O$-bond MO given by Eq. (15.114) is $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$. The unpaired electrons created by bond breakage of the double $C=O$ bond requires that two times the $O2p$ AO magnetic energy E_{mag} (Eq. (15.60)) be subtracted from the total energy to give $E_D\left(Group\right)\ (eV)$ for $C=O$.

As in the case with aldehydes, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C=O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is –2.69893 eV which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of

the energy contributions corresponding to a double bond, $-1.13379\,eV$ (Eq. (14.247)), and a triple bond, $-1.56513\,eV$ (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the $C-C(O)$ bond in addition to the pair involved directly in the double bond with O. Consequently, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-C(O)$-bond MO is $-1.44915\,eV$, corresponding to the energy contributions of the two $C2sp^3$ HOs to the single bond that are equivalent to those of methyl groups, $-0.72457\,eV$ (Eq. (14.151)). Since there are two $C-C(O)$ bonds in ketones versus one in aldehydes, $C_{1o}=C_1$ in Eq. (15.52) for each $C-C(O)$ ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.55)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl ketones determined using Eqs. (15.79-15.108) are given in Table 15.98.

Table 15.93. The symbols of functional groups of alkyl ketones.

Functional Group	Group Symbol
C=O	$C=O$
C-C(O)	$C-C(O)$
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.94. The geometrical bond parameters of alkyl ketones and experimental values [1].

Parameter	$C=O$ Group	$C-C(O)$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.312172	2.04740	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.14550	1.43087	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.21235	1.51437	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.213 (acetone) 1.219 (2-butanone)	1.520 (acetone) 1.518 (2-butanone)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,e\ (a_0)$	0.64002	1.46439	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.87298	0.69887	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.95. The MO to HO intercept geometrical bond parameters of alkyl ketones. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\ (a_0)$	$d_2\ (a_0)$
$R'C_eH_2\left(RC_bH_2\right)C_a=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		136.09	43.91	65.72	0.53955	0.60595
$R'C_eH_2\left(RC_bH_2\right)C_a=O$	C'_a	-1.34946	-0.72458	-0.72458	0	-154.41430	0.91771	0.77199	-17.62437	-17.43350	133.02	46.98	61.86	0.61878	0.52672
$H_3C_b-C_a(O)(R')$	C'_b	-0.72458	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	73.62	106.38	34.98	1.67762	0.246675
$RH_2C_e-H_2C_b-C_a(O)(R')$	C'_b	-0.72458	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	67.40	112.60	31.36	1.74821	0.31734
$C'-H\ (CH_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ (CH_2)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (CH)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC_bH_2CH_2-$ ($C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC_bH_2CH_2-$ ($C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC_b\left(H_2C_e-R'\right)HCH_2-$ ($C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC_b\left(H_2C_e-R'\right)HCH_2-$ ($C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC_b\left(H_2C_e-R'\right)HCH_2-$ ($C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.96. The energy parameters (eV) of functional groups of alkyl ketones.

Parameters	$C=O$ Group	$C-C(O)$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	0	0	1	1	0	0	0	1	1	0
c_4	4	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1n}	0.5	1	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2n}	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-109.17602	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.75521	9.50874	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	41.60126	7.37432	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ne} (eV)	-20.80063	-3.68716	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(xo\ no)$ (eV)	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2xo}(xo\ no)$ (eV)	-1.34946	0	0	0	0	0	0	0	0	0	0
$E_T(xo\text{-}no)$ (eV)	1.34946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2xo)$ (eV)	-63.27071	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(xo)$ (eV)	-65.96966	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	57.0928	16.4962	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	37.57947	10.85807	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D$ (eV)	-0.40003	-0.21568	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kvib}$ (eV)	0.21462 [27]	0.14655 [28]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{osc}$ (eV)	-0.29272	-0.14240	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(cinap)$ (eV)	-66.55510	-33.22692	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{mutual}(c,xo\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{mutual}(c,xo\ no)$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(cinap)$ (eV)	7.78672	3.95714	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.97. The total bond energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by (15.57).

Formula	Name	$C=O$ Group	$C-C(O)$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_6O	Acetone	1	2	2	0	0	0	0	0	0	0	0	0	40.68472	40.672	-0.00031
C_4H_8O	2-Butanone	1	2	2	1	0	1	0	0	0	0	0	0	52.84242	52.84	-0.00005
$C_5H_{10}O$	2-Pentanone	1	2	2	2	0	2	0	0	0	0	0	0	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Pentanone	1	2	2	2	0	2	0	0	0	0	0	0	65.00012	64.997	-0.00005
$C_5H_{10}O$	3-Methyl-2-butanone	1	2	3	0	1	0	2	0	0	0	0	0	65.10101	65.036	-0.00099
$C_6H_{12}O$	2-Hexanone	1	2	2	2	0	3	0	0	0	0	0	0	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	1	2	2	3	0	3	0	0	0	0	0	0	77.15782	77.138	-0.00025
$C_6H_{12}O$	2-Methyl-3-pentanone	1	2	3	1	1	1	2	0	0	0	0	0	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	1	2	4	0	0	0	0	3	0	0	0	-2	77.29432	77.273	-0.00028
$C_7H_{14}O$	3-Heptanone	1	2	2	4	0	4	0	0	0	0	0	0	89.31552	89.287	-0.00032
$C_7H_{14}O$	4-Heptanone	1	2	0	4	0	4	0	0	0	0	0	0	89.31552	89.299	-0.00018
$C_7H_{14}O$	2,2-Dimethyl-3-pentanone	1	2	4	1	0	1	0	3	0	0	0	-2	89.45202	89.458	0.00007
$C_7H_{14}O$	2,4-Dimethyl-3-pentanone	1	2	4	0	2	0	4	0	0	0	0	0	89.51730	89.434	-0.00093
$C_8H_{16}O$	2,2,4-Trimethyl-3-pentanone	1	2	5	0	1	0	2	3	0	0	0	-2	101.71061	101.660	-0.00049
$C_9H_{18}O$	2-Nonanone	1	2	2	6	0	6	0	0	0	0	0	0	113.63092	113.632	0.00001
$C_9H_{18}O$	5-Nonanone	1	2	2	6	0	6	0	0	0	0	0	0	113.63092	113.675	0.00039
$C_9H_{18}O$	2,6-Dimethyl-4-heptanone	1	2	4	2	2	0	6	0	0	0	0	0	113.77604	113.807	0.00027

Table 15.98. The bond angle parameters of alkyl ketones and experimental values [1]. In the calculation of θ_r, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_bC_a(O)C_c$	2.86175	2.86175	4.8477	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				115.77	116.0 (acetone)
$\angle C_dC_bC_a(O)$	2.91547	2.86175	4.8374	-16.68412 C_d	25	-16.68412 C_a	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				113.71	113.5 (2-butanaone)
$\angle C_bC_aO$	2.86175	2.29100	4.5166	-15.55033	5	-13.61806	O	0.87495	0.85395 (Eq. (15.114))	1	1	1	0.86445	-1.44915				122.07	121.9 (2-butanaone)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

CARBOXYLIC ACIDS ($C_nH_{2n}O_2$, $n=1,2,3,4,5...\infty$)

The alkyl carboxylic acids, $C_nH_{2n}O_2$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formic acid has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group. All carboxylic acids further comprise a $C-OH$ moiety that comprises $C-O$ and OH functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that the energy of the $C-H$ MO is matched to the carbon-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$ group. The alkyl carboxylic acid $C=O$ and $C-C(O)$ groups are equivalent to those given in the Aldehydes section except that $\overline{E}_{Kvib}$ is that of a carboxylic acid. The formic acid $C=O$ group is solved equivalently to that of the alkyl carboxylic acid group, except that $\Delta E_{H_2MO}(AO/HO)$ and $E_T\left(atom-atom,msp^3.AO\right)$ correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the $C=O$ MO due to the presence of a H bound to the carbonyl carbon. Also, $\overline{E}_{Kvib}$ is that corresponding to formic acid. The $C-O$ and OH groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the $C-O$ MO is matched to that of the $C=O$ group and $\overline{E}_{Kvib}$ is that of a carboxylic acid. $\Delta E_{H_2MO}(AO/HO)$ of the $C-O$ group is equal to $E_T\left(atom-atom,msp^3.AO\right)$ of the alkyl $C=O$ group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C=O$-bond MO in Eq. (15.52) of alky carboxylic acids due to the charge donation from the C and O

atoms to the MO is $-2.69893\ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, $-1.13379\ eV$ (Eq. (14.247)), and a triple bond, $-1.56513\ eV$ (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl $C2sp^3$ HO electron with the O of the $C-O$-bond MO in addition to the pair involved directly in the double bond with the carbonyl O.

$E_T\left(atom-atom,msp^3.AO\right)$ of the formic acid $C=O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-3.58557\ eV$. This is also an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a triple bond, $-1.56513\ eV$ (Eq. (14.342)), and a quadruple bond, $-2.02043\ eV$ (Eqs. (15.18-15.21) with $s=4$)) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a H bound to the carbonyl carbon.

$E_T\left(atom-atom,msp^3.AO\right)$ of the carboxylic acid $C-C(O)$ group is equivalent to that of alkanes and aldehydes, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the carboxylic acid. As in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

$E_T\left(atom-atom,msp^3.AO\right)$ of the carboxylic acid $C-O$ group is equivalent to that of alkyl alcohols, $-1.85836\ eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513). $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$ group matches that of the $C-C(O)$ group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired

electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table 15.104.

Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

Functional Group	Group Symbol
CH (formic acid) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formic acid)	$C=O$ (i)
C=O (alkyl carboxylic acid)	$C=O$ (ii)
(O)C-O	$C-O$
OH group	OH
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.100. The geometrical bond parameters of alkyl carboxylic acids and experimental values [1].

Parameter	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	OH Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.61341	2.04740	1.290799	1.29907	1.73490	1.26430	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.03711	1.43087	1.13613	1.13977	1.31716	0.91808	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.09763	1.51437	1.20243	1.20628	1.39402	0.971651	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.097 (formic acid)	1.520 (acetic acid)	1.202 (formic acid)	1.214 (acetic acid)	1.393 (methyl formate)	0.972 (formic acid)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1 122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.23591	1.46439	0.61267	0.62331	1.12915	0.86925	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.64281	0.69887	0.88018	0.87737	0.75921	0.72615	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.101. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acids. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	r_{match} (a_0)	r_{bond} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C'2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$RC_a(O)O-H$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		115.09	64.91	64.12	0.55182	0.36625
$HC_a(O)-OH$ ($C=O$ (i))	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		101.32	78.68	48.58	1.14765	0.16950
$HC_a(O)-OH$ ($C=O$ (i))	C'_a	-0.92918	-1.79278	0	0	-154.33765	0.91771	0.77536	-17.54772	-17.35685	93.94	86.06	43.24	1.26386	0.05329
$RH_2C_bC_a(O)-OH$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		101.32	78.68	48.58	1.14765	0.16950
$RH_2C_bC_a(O)-OH$	C'_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	91.96	88.04	41.90	1.29138	0.02578
$HC_a(OH)=O$ ($C=O$ (i))	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$HC_a(OH)=O$ ($C=O$ (i))	C'_a	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	135.24	44.76	63.02	0.58561	0.55053
$RC_bH_2C_a(OH)=O$ ($C=O$ (ii))	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RC_bH_2C_a(OH)=O$ ($C=O$ (ii))	C'_a	-1.34946	-0.92918	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	133.47	46.53	61.46	0.62072	0.51905
$H-C(O)OH$ ($C'H$ (i))	C'	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	69.89	110.11	36.09	1.30373	0.26662
$RH_2C_b-C_a(O)OH$	C'_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	56.25	123.75	25.37	1.85002	0.41915
$H_2C_b-C_a(O)OH$	C'_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$RH_2C_cH_2C_b-C_a(O)OH$	C'_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H\ (C'H_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.25564	0.18708
$C'-H\ (C'H_2)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (C'H)$ (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_2C'_aC_bH_2C'H_2-$ ($C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_2C'_aC_bH_2C'H_2-$ ($C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC_b(H_2C_c-R')HC'H_2-$ ($C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a(R'-H_2C_d)C_b(R''-H_2C_e)C'H_2-$ ($C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC_b(H_2C_c-R')HC'H_2-$ ($C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a(R'-H_2C_d)C_b(R''-H_2C_e)C'H_2-$ ($C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC_b(H_2C_c-R')HC'H_2-$ ($C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a(R'-H_2C_d)C_b(R''-H_2C_e)C'H_2-$ ($C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.102. The energy parameters (eV) of functional groups of alkyl carboxylic acids.

Parameters	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	OH Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	2	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.85395	0.85395	0.85395	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	2	2	0	1	0	1	1	0	0	0	1	1	0
c_4	1	2	4	4	2	1	1	1	1	2	2	2	2	2	2
c_5	1	0	0	0	0	1	3	2	1	0	0	0	0	0	0
C_{1n}	0.75	1	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2n}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-36.74167	-30.19634	-112.61934	-111.25473	-35.08488	-40.92709	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	13.11890	9.50874	23.95107	23.87467	10.32968	14.81988	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	11.38634	7.37432	43.62389	42.82081	10.11150	16.18567	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ne} (eV)	-5.69317	-3.68716	-21.81195	-21.41040	-5.05575	-8.09284	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(no\ no)$ (eV)	-14.63489	-14.63489	0	0	-14.63489	-13.6181	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_NO}(no\ no)$ (eV)	-0.92918	0	-3.58557	-2.69893	-2.69893	0	0	0	0	0	0	0	0	0	0
$E_x(no\ no)$ (eV)	-13.70571	-14.63489	3.58557	2.69893	-11.93596	-13.6181	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_p(no\ no)$ (eV)	-31.63530	-31.63534	-63.27075	-63.27074	-31.63541	-31.63247	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_x\left(atom-atom, msp^3.AO\right)$ (eV)	0	-1.85836	-3.58557	-2.69893	-1.85836	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_p(no)$ (eV)	-31.63537	-33.49373	-66.85630	-65.96966	-33.49373	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	26.0575	23.3291	60.9581	59.4034	24.3637	44.1776	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	17.15150	15.35563	40.12366	39.10034	16.03660	29.07844	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_n$ (eV)	-0.25920	-0.25966	-0.41891	-0.40804	-0.26535	-0.33749	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Abb}$ (eV)	0.35532 (Eq. (13.458))	0.10502 [29]	0.21945 [30]	0.21077 [12]	0.14010 [31]	0.46311 [17-18]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{exc}$ (eV)	-0.08153	-0.20715	-0.30918	-0.30266	-0.19530	-0.10594	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_p(comp)$ (eV)	-31.71690	-33.70088	-67.47466	-66.57498	-33.68903	-31.74130	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{method}(e_1\ no\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{method}(e_2\ no\ no)$ (eV)	-13.59844	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(comp)$ (eV)	3.48357	4.43110	8.70628	7.80660	4.41925	4.41035	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.103. The total bond energies of alkyl carboxylic acids calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(comp)$ (eV) values based on composition is given by (15.57).

Formula	Name	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	OH Group	CH_3	CH_2	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_2O_2	Formic acid	1	0	1	0	1	1	0	0	0	0	0	0	0	0	0	0	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	0	1	0	1	1	1	1	0	0	0	0	0	0	0	0	0	33.55916	33.537	-0.00066
$C_3H_6O_2$	Propanoic acid	0	1	0	1	1	1	1	1	0	1	0	0	0	0	0	0	45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	0	1	0	1	1	1	1	2	0	2	0	0	0	0	0	0	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	0	1	0	1	1	1	1	3	0	3	0	0	0	0	0	0	70.03226	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	0	1	0	1	1	1	2	1	1	0	3	0	0	0	0	0	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	0	1	0	1	1	1	3	0	0	0	0	3	0	0	0	-1	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	0	1	0	1	1	1		4	0	4	0	0	0	0	0	0	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	0	1	0	1	1	1	1	5	0	5	0	0	0	0	0	0	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	0	1	0	1	1	1	1	6	0	6	0	0	0	0	0	0	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	0	1	0	1	1	1	1	7	0	7	0	0	0	0	0	0	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	0	1	0	1	1	1	1	8	0	8	0	0	0	0	0	0	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	0	1	0	1	1	1	1	10	0	10	0	0	0	0	0	0	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	0	1	0	1	1	1	1	12	0	12	0	0	0	0	0	0	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	0	1	0	1	1	1	1	13	0	13	0	0	0	0	0	0	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	0	1	0	1	1	1	1	14	0	14	0	0	0	0	0	0	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	0	1	0	1	1	1	1	16	0	16	0	0	0	0	0	0	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	0	1	0	1	1	1	1	18	0	18	0	0	0	0	0	0	252.39776	252.514	0.00046

Table 15.104. The bond angle parameters of alkyl carboxylic acids and experimental values [1] In the calculation of θ_e, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_n)	$2c'$ Bond 2 (a_n)	$2c'$ Terminal Atoms (a_n)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C'_1	C'_2	c_1	c'_2	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aO_a$ (CH (i); $C=O$ (i))	2.06598	2.27227	3.8816	-15.55033 C_a	5	-13.61806	O	0.87495	0.85395 (Eq. (15.114))	0.75	1	0.75	0.97600	0				126.88	124.1 (formic acid)
$\angle HC_aO_b$ (CH (i))	2.06598	2.63431	3.8816	-15.55033 C_a	5	-13.61806	O	0.87495	0.85395 (Eq. (15.114))	0.75	1	0.75	0.97600	0				110.76	
$\angle O_aC_aO_b$	2.27227	2.63431	4.3243	-16.61853 O_a	23	-15.75493 O_b	7	0.81871	0.86359	1	1	1	0.84115	-1.44915				123.44	124.9 (formic acid)
$\angle C_aO_bH$ (CH (i); $C=O$ (i))	2.63431	1.83616	3.6405	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				107.71	106.3 (formic acid)
$\angle C_bC_aO_a$	2.86175	2.27954	4.5826	-16.68411	24	-13.61806	O	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				125.70	126.6 (acetic acid)
$\angle C_bC_aO_b$	2.86175	2.63431	4.4944	-15.75493	7	-13.61806	O	0.86359	0.85395 (Eq. (15.114))	1	1	1	0.85877	-1.44915				109.65	110.6 (acetic acid)
$\angle O_aC_aO_b$	2.27954	2.63431	4.3818	-16.17521 O_a	12	-15.75493 O_b	7	0.84115	0.86359	1	1	1	0.85257	-1.44915				126.03	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493		H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

CARBOXYLIC ACID ESTERS ($C_nH_{2n}O_2$, $n=1,2,3,4,5...\infty$)

The alkyl carboxylic acid esters, $C_nH_{2n}O_2$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formic acid ester has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group. All carboxylic acid esters further comprise a COR moiety that comprises a $C-O$ functional group and three types of $O-R$ functional groups, one for R comprising methyl, one for R comprising an alkyl ester group of a formate, and one for R comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The CH functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester $C=O$ and $C-C(O)$ groups are equivalent to those given in the Carboxylic Acids section. The formic acid ester $C=O$ group is equivalent to that given in the Carboxylic Acids section except that $\overline{E}_{Kvib}$ is that corresponding to a formic acid ester. The $C-O$ group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state, $\overline{E}_D$ (eV) and $\overline{E}_{Kvib}$, are those of a carboxylic acid ester. As in the case with the alkyl ethers, each $O-C$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $O-C$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $O-C$-bond MO given by Eq. (15.114) is $c_2\left(C2sp^3 HO\ to\ O\right)=0.85395$.

$E_T\left(atom-atom,msp^3.AO\right)$ (Eq. (15.52)) of (1) the $C=O$ group of alky carboxylic acid esters, (2) the $C=O$ group of formic acid esters, (3) the alkyl carboxylic acid ester $C-C(O)$ group, and (4) the carboxylic acid ester $C-O$ group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are $-2.69893\,eV$, $-3.58557\,eV$, $-1.85836\,eV$, and $-1.85836\,eV$, respectively. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-O$ group matches that of the $C-C(O)$ group. Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52) for the $C-C(O)$ group.

$E_T\left(atom-atom,msp^3.AO\right)$ of the $O-C$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.13379\,eV$ for the $O-CH_3$ group of formate and alkyl carboxylates, $-1.44915\,eV$ for the $O-R$ group of alkyl carboxylates, and $-1.85836\,eV$ for the $O-R$ group of alkyl formates, where R is an alkyl group. Each is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), the $C2sp^3$ HO of the methyl or alkyl ester group, and the carbonyl carbon. The increasing energy contributions to the single bond correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are $-1.13379\,eV$ (Eq. (14.247)), two times $-0.72457\,eV$ (Eq. (14.151)), and two times $-0.92918\,eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table 15.105. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.108 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.79-15.108) are given in Table 15.110.

Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

Functional Group	Group Symbol
CH (formic acid ester) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formic acid ester)	$C=O$ (i)
C=O (alkyl carboxylic acid ester)	$C=O$ (ii)
(O)C-O	$C-O$
O-CH_3	$O-C$ (i)
O-R (formic acid ester)	$O-C$ (ii)
O-R (alkyl acid ester)	$O-C$ (iii)
OH group	OH
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.106. The geometrical bond parameters of alkyl carboxylic acid esters and experimental values [1].

Parameter	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	$O-C$ (i) Group	$O-C$ (ii) Group	$O-C$ (iii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.61341	2.04740	1.290799	1.29907	1.73490	1.82683	1.78255	1.80717	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.03711	1.43087	1.13613	1.13977	1.31716	1.35160	1.33512	1.34431	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.09763	1.51437	1.20243	1.20628	1.39402	1.43047	1.41303	1.42276	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.101 (methyl formate)	1.520 (acetic acid)	1.206 (methyl formate)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.08 (methyl formate) 1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.23591	1.46439	0.61267	0.62331	1.12915	1.22901	1.18107	1.20776	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.64281	0.69887	0.88018	0.87737	0.75921	0.73986	0.74900	0.74388	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.107. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid esters. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RC_a(O)O-C_bH_3$ $(O-C$ (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183		90.63	89.37	42.70	1.34246	0.00914
$RC_a(O)O-C_bH_3$ $(O-C$ (i))	C_b	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	95.01	84.99	45.76	1.27445	0.07716
$HC_a(O)O-C_bH_2C_cH_2R$ $(O-C$ (ii))	O	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68412		93.09	86.91	43.59	1.29113	0.04399
$HC_a(O)O-C_bH_2C_cH_2R$ $(O-C$ (ii))	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	93.09	86.91	43.59	1.29113	0.04399
$R'C_a(O)O-C_bH_2C_cH_2R$ $(O-C$ (iii))	O	-0.92918	-0.72457	0	0		1.00000	0.82562	-16.47951		91.72	88.28	43.10	1.31951	0.02480
$R'C_a(O)O-C_bH_2C_cH_2R$ $(O-C$ (iii))	C_b	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	91.72	88.28	43.10	1.31951	0.02480
$HC_a(O)-OC_bH_3$ $(C=O$ (i)) $(O-C$ (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183		98.97	81.03	46.82	1.18716	0.13000
$HC_a(O)-OC_bH_3$ $(C=O$ (i)) $(O-C$ (i))	C_a	-0.92918	-1.79278	0	0	-154.33765	0.91771	0.77536	-17.54772	-17.35685	93.94	86.06	43.24	1.26386	0.05329
$HC_a(O)-OR$ $(C=O$ (i)) $(O-C$ (ii))	O	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68412		97.48	82.52	45.73	1.21100	0.10616
$HC_a(O)-OR$ $(C=O$ (i)) $(O-C$ (ii))	C_a	-1.79278	-0.92918	0	0	-154.33765	0.91771	0.77536	-17.54772	-17.35685	93.94	86.06	43.24	1.26386	0.05329
$R'H_2C_bC_a(O)-OC_bH_3$ $(C=O$ (ii)) $(O-C$ (i))	O	-0.92918	-0.56690	0	0		1.00000	0.83360	-16.32183		98.97	81.03	46.82	1.18716	0.13000
$R'H_2C_bC_a(O)-OC_bH_3$ $(C=O$ (ii)) $(O-C$ (i))	C_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	91.96	88.04	41.90	1.29138	0.02578
$R'H_2C_bC_a(O)-OC_bH_2C_cH_2R$ $(C=O$ (ii)) $(O-C$ (iii))	O	-0.92918	-0.72457	0	0		1.00000	0.82562	-16.47951		98.32	81.68	46.34	1.19766	0.11949
$R'H_2C_bC_a(O)-OC_bH_2C_cH_2R$ $(C=O$ (ii)) $(O-C$ (iii))	C_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84271	91.96	88.04	41.90	1.29138	0.02578
$HC_a(OR)=O$ $(C=O$ (i))	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$HC_a(OR)=O$ $(C=O$ (i))	C_a	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	135.24	44.76	63.02	0.58561	0.55053
$R'C_bH_2C_a(OR)=O$ $(C=O$ (ii))	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$R'C_bH_2C_a(OR)=O$ $(C=O$ (ii))	C_a	-1.34946	-0.92918	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84272	133.47	46.53	61.46	0.62072	0.51905
$H-C(O)OR$ $(CH$ (i))	C	-1.79278	-0.92918	0	0	-154.33766	0.91771	0.77536	-17.54772	-17.35685	69.89	110.11	36.09	1.30373	0.26662
$R'H_2C_b-C_a(O)OR$	C_a	-0.92918	-1.34946	-0.92918	0	-154.82352	0.91771	0.75447	-18.03358	-17.84272	56.25	123.75	25.37	1.85002	0.41915
$H_3C_b-C_a(O)OR$	C_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$R'H_2C_cH_2C_b-C_a(O)OR$	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C-H\left(CH_3\right)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_2\right)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H$ (C'H) (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37526
$H_2C_aC_bH_2C'H_2-$ (C'–C' (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_2C_aC_bH_2C'H_2-$ (C'–C' (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_cC_d\left(H_2C_e-R'\right)HC'H_2-$ (C'–C' (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_cC_d\left(R''-H_2C_e\right)C_b\left(R''-H_2C_a\right)C'H_2-$ (C'–C' (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$tert\text{-}C_cC_d\left(H_2C_e-R'\right)HC'H_2-$ (C'–C' (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tert\text{-}C_c\left(R''-H_2C_d\right)C_b\left(R''-H_2C_a\right)C'H_2-$ (C'–C' (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tert\text{-}C_cC_d\left(H_2C_e-R'\right)HC'H_2-$ (C'–C' (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$tert\text{-}C_c\left(R''-H_2C_d\right)C_b\left(R''-H_2C_a\right)C'H_2-$ (C'–C' (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.108. The energy parameters (eV) of functional groups of alkyl carboxylic acid esters.

Parameters	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-O$ Group	$O-C$ (i) Group	$O-C$ (ii) Group	$O-C$ (iii) Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	2	2	1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.85395	0.85395	0.85395	0.85395	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	2	2	0	0	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	4	4	2	2	2	2	1	1	1	2	2	2	2	2	2
c_5	1	0	0	0	0	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.75	1	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_r (eV)	-36.74167	-30.19634	-112.61934	-111.25473	-35.08488	-32.67173	-33.78830	-33.15757	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	13.11890	9.50874	23.95107	23.87467	10.32968	10.06642	10.19070	10.12103	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	11.38634	7.37432	43.62389	42.82081	10.11150	8.94219	9.47754	9.17389	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_w (eV)	-5.69317	-3.68716	-21.81195	-21.41040	-5.05575	-4.47110	-4.73877	-4.58695	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\pi no)$ (eV)	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{\pi_2 NO}(\pi no)$ (eV)	-0.92918	0	-3.58557	-2.69893	-2.69893	-1.13379	-1.85836	-1.44915	0	0	0	0	0	0	0	0	0
$E_\gamma(\pi no)$ (eV)	-13.70571	-14.63489	3.58557	2.69893	-11.93596	-13.50110	-12.77653	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(\pi_2 NO)$ (eV)	-31.63530	-31.63534	-63.27075	-63.27074	-31.63541	-31.63531	-31.63536	-31.63533	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	0	-1.85836	-3.58557	-2.69893	-1.85836	-1.13379	-1.85836	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(\pi no)$ (eV)	-31.63537	-33.49373	-66.85630	-65.96966	-33.49373	-32.76916	-33.49373	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	26.0575	23.3291	60.9581	59.4034	12.7926	21.4553	22.7749	12.0329	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	17.15150	15.35563	40.12366	39.10034	8.42030	14.12224	14.99085	7.92028	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.25920	-0.25966	-0.41891	-0.40804	-0.19228	-0.24362	-0.25655	-0.18420	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{kvdA}$ (eV)	0.35532 (Eq. (13.458))	0.10502 [29]	0.21747 [32]	0.21077 [12]	0.14965 [32]	0.11469 [32]	0.11469 [32]	0.16118 [4]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{osc}$ (eV)	-0.08153	-0.20715	-0.31017	-0.30266	-0.11745	-0.18628	-0.19921	-0.10361	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{corr} (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(group)$ (eV)	-31.71690	-33.70088	-67.47664	-66.57498	-33.61118	-32.95544	-33.69294	-33.18813	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(\epsilon_1, no\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(\epsilon_2, no\ no)$ (eV)	-13.59844	0	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{ph}(group)$ (eV)	3.48357	4.43110	8.70826	7.80660	4.34141	3.68566	4.42316	3.91835	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.109. The total bond energies of alkyl carboxylic acid esters calculated using the functional group composition and the energies of Table 15.108 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_0(Group)$ (eV) values based on composition is given by (15.57).

Formula	Name	C−H (i) Group	C−C(O) Group	C=O (i) Group	C=O (ii) Group	C−O Group	O−C (i) Group	O−C (ii) Group	O−C (iii) Group	CH_3	CH_2	CH (ii)	C−C (a)	C−C (b)	C−C (c)	C−C (d)	C−C (e)	C−C (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_4O_2$	Methyl formate	1	1	1	0	1	1	0	0	1	0	0	0	0	0	0	0	0	0	32.71076	32.762	0.00156
$C_3H_6O_2$	Methyl acetate	0	1	1	1	1	0	0	0	2	0	0	0	0	0	0	0	0	0	45.24849	45.288	0.00087
$C_6H_{12}O_2$	Methyl pentanoate	0	1	1	1	1	0	0	0	2	3	0	3	0	0	0	0	0	0	81.72159	81.726	0.00005
$C_7H_{14}O_2$	Methyl hexanoate	0	1	1	1	1	0	0	0	2	4	0	4	0	0	0	0	0	0	93.87929	93.891	0.00012
$C_8H_{16}O_2$	Methyl heptanoate	0	1	1	1	1	0	0	0	2	5	0	5	0	0	0	0	0	0	106.03699	106.079	0.00040
$C_9H_{18}O_2$	Methyl octanoate	0	1	1	1	1	0	0	0	2	6	0	6	0	0	0	0	0	0	118.19469	118.217	0.00018
$C_{10}H_{20}O_2$	Methyl nonanoate	0	1	1	1	1	0	0	0	2	7	0	7	0	0	0	0	0	0	130.35239	130.373	0.00016
$C_{11}H_{22}O_2$	Methyl decanoate	0	1	1	1	1	0	0	0	2	8	0	8	0	0	0	0	0	0	142.51009	142.523	0.00009
$C_{12}H_{24}O_2$	Methyl undecanoate	0	1	1	1	1	0	0	0	2	9	0	9	0	0	0	0	0	0	154.66779	154.677	0.00006
$C_{13}H_{26}O_2$	Methyl dodecanoate	0	1	1	1	1	0	0	0	2	10	0	10	0	0	0	0	0	0	166.82549	166.842	0.00010
$C_{14}H_{28}O_2$	Methyl tridecanoate	0	1	1	1	1	0	0	0	2	11	0	11	0	0	0	0	0	0	178.98319	179.000	0.00009
$C_{15}H_{30}O_2$	Methyl tetradecanoate	0	1	1	1	1	0	0	0	2	12	0	12	0	0	0	0	0	0	191.14089	191.170	0.00015
$C_{16}H_{32}O_2$	Methyl pentadecanoate	0	1	1	1	1	0	0	0	2	13	0	13	0	0	0	0	0	0	203.29859	203.356	0.00028
$C_4H_8O_2$	Propyl formate	0	1	1	1	1	0	0	0	1	2	1	2	0	0	0	0	0	0	57.76366	57.746	-0.00030
$C_4H_8O_2$	Ethyl acetate	0	1	0	1	1	0	0	1	2	1	0	1	0	0	0	0	0	0	57.63888	57.548	-0.00157
$C_5H_{10}O_2$	Isopropyl acetate	0	1	0	0	1	0	0	1	3	0	1	0	2	0	0	0	0	0	69.89747	69.889	-0.00013
$C_5H_{10}O_2$	Ethyl propanoate	0	1	0	1	1	0	0	1	2	2	0	2	0	0	0	0	0	0	69.79658	69.700	-0.00139
$C_6H_{12}O_2$	Butyl acetate	0	1	0	1	1	0	0	1	2	3	0	3	0	0	0	0	0	0	81.95428	81.873	-0.00099
$C_6H_{12}O_2$	t-Butyl acetate	0	1	0	1	1	0	0	1	4	0	0	0	0	3	0	0	0	0	82.23881	82.197	-0.00051
$C_6H_{12}O_2$	Methyl 2,2-dimethylpropanoate	0	1	0	1	1	1	0	0	4	0	0	0	0	3	0	0	0	-1	82.00612	81.935	-0.00087
$C_7H_{14}O_2$	Ethyl pentanoate	0	1	0	1	1	0	0	1	2	6	0	6	0	0	0	0	0	0	94.11198	94.033	-0.00084
$C_7H_{14}O_2$	Ethyl 3-methylbutanoate	0	1	0	1	1	0	0	1	3	2	1	1	3	0	0	0	0	0	94.18454	94.252	0.00072
$C_7H_{14}O_2$	Ethyl 2,2-dimethylpropanoate	0	1	0	1	1	0	0	1	4	1	0	1	0	3	0	0	0	-1	94.39651	94.345	-0.00054
$C_8H_{16}O_2$	Isobutyl isobutanoate	0	1	0	1	1	0	0	1	4	1	2	0	5	0	0	0	0	0	106.44313	106.363	-0.00075
$C_8H_{16}O_2$	Propyl pentanoate	0	1	0	1	1	0	0	1	2	5	0	5	0	0	0	0	0	0	106.26968	106.267	-0.00003
$C_8H_{16}O_2$	Isopropyl pentanoate	0	1	0	1	1	0	0	1	3	3	1	3	2	0	0	0	0	0	106.37057	106.384	0.00013
$C_9H_{18}O_2$	Butyl pentanoate	0	1	0	1	1	0	0	1	2	6	0	6	0	0	0	0	0	0	118.42738	118.489	0.00052
$C_9H_{18}O_2$	sec-Butyl pentanoate	0	1	0	1	1	0	0	1	3	4	1	4	2	0	0	0	0	0	118.52827	118.624	0.00081
$C_9H_{18}O_2$	Isobutyl pentanoate	0	1	0	1	1	0	0	1	3	4	1	3	3	0	0	0	0	0	118.49994	118.576	0.00064

Table 15.110. The bond angle parameters of alkyl carboxylic acid esters and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,nsp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{C_{coulombic}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{C_{coulombic}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_bO_b$ (CH (i); $C=O$ (i))	2.09711	2.70321	3.9463	-15.75493 C_b	7	-13.61806	O	0.86359	0.85395 (Eq. (15.114))	0.75	1	0.75	0.98884	0				109.95	110 (methyl formate)
$\angle O_aC_aO_b$ (CH (i); $C=O$ (i))	2.27227	2.63431	4.4045	-16.61853 O_a	23	-16.68412 O_b	25	0.81871	0.81549	1	1	1	0.81710	-1.65376				127.56	127 (methyl formate)
$\angle C_bO_bC_a$ (CH (i); $C=O$ (i))	2.70321	2.63431	4.4833	-16.32183 C_b	16	-18.47690 C_a	50	0.83360	0.73637	1	1	1	0.78498	-1.85836				114.27	114 (methyl formate)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

AMIDES ($C_nH_{2n+1}NO$, $n=1,2,3,4,5...\infty$)

The alkyl amides, $C_nH_{2n+1}NO$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formamide has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group that is equivalent to that of the CH (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso-CH group of branched-chain-alkyl portion of the alkyl amide except that E_{mag} (Eq. (15.58)) is not subtracted from $E_D(Group)$. All amides further comprise a $C-NH_2$ moiety that comprises a NH_2 functional group and two types of $C-N$ functional groups, one for formamide and the other for alkyl amides ($RC(O)NH_2$ where R is alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The NH_2 functional group was solved in the Dihydrogen Nitride (NH_2) section except that the energy of the $N-H$ MO is matched to the nitrogen-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-N$ group. Both alkyl amide $C=O$ groups and the $C-C(O)$ group are equivalent to those given in the Carboxylic Acid Esters section except that $\overline{E}_{Kvib}$ of the $C-C(O)$ group is matched to that of an amide. The $C-N$ groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the $C-N$ MO is matched to that of the $C=O$ group and $\overline{E}_{Kvib}$ is that of a amide. $\Delta E_{H_2MO}(AO/HO)$ of the $C-N$ group is equal to $E_T\left(atom-atom,msp^3.AO\right)$ of the alkyl $C=O$ and $C-N$ groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each $C-N$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of

electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the $C-N$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the $C-N$-bond MO given by Eq. (15.114) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$.

$E_T\left(atom-atom,msp^3.AO\right)$ (Eq. (15.52)) of the $C=O$ group of alky amides and the $C=O$ group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are $-2.69893\ eV$ and $-3.58557\ eV$, respectively.

$E_T\left(atom-atom,msp^3.AO\right)$ of the amide $C-C(O)$ group is the same as alkanes, aldehydes, carboxylic acids, and carboxylic acid esters, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

In order to match energy throughout the chain of the amide molecule, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.65376\ eV$. It is based on the energy match between the $C2sp^3$ HO of the carbonyl and the primary amino group NH_2. It is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) which matches the contiguous $C-C(O)$ or $HC(O)$ group and $-0.72457\ eV$ (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.114 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.116.

Table 15.111. The symbols of functional groups of alkyl amides.

Functional Group	Group Symbol
CH (formamide) group	$C-H$ (i)
C-C(O)	$C-C(O)$
C=O (formamide)	$C=O$ (i)
C=O (alkyl amide)	$C=O$ (ii)
(O)C-N (formamide)	$C-N$ (i)
(O)C-N (alkyl amide)	$C-N$ (ii)
NH_2 group	NH_2
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH (alkyl) group	$C-H$ (ii)
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.112. The geometrical bond parameters of alkyl amides and experimental values [1].

Parameter	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH_2 Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.67465	2.04740	1.290799	1.29907	1.70920	1.75370	1.32297	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.05661	1.43087	1.13613	1.13977	1.30736	1.32427	0.97065	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.11827	1.51437	1.20243	1.20628	1.38365	1.40155	1.02729	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.125 (formamide)	1.519 (acetamide) 1.520 (N-methylacetamide)	1.212 (formamide)	1.220 (acetamide) 1.225 (N-methylacetamide)	1.368 (formamide)	1.380 (acetamide)	1.027 (formamide) 1.022 (acetamide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,c\ (a_0)$	1.29924	1.46439	0.61267	0.62331	1.10098	1.14968	0.89894	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.63095	0.69887	0.88018	0.87737	0.76490	0.75513	0.73369	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.113. The MO to HO intercept geometrical bond parameters of alkyl amides. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, nsp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RC(O)N(H)-H$ ($C=O$ (i) and (ii))	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		113.90	66.10	62.13	0.61843	0.35222
$HC(O)-NH_2$ ($C=O$ (i)) ($C-N$ (i))	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		103.93	76.07	50.02	1.09814	0.20922
$HC(O)-NH_2$ ($C=O$ (i)) ($C-N$ (i))	C'	-0.82688	-1.79278	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	96.81	83.19	44.70	1.21492	0.09244
$RH_2C_bC_a(O)-NH_2$ ($C=O$ (ii)) ($C-N$ (ii))	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		100.14	79.86	48.10	1.17127	0.15300
$RH_2C_bC_a(O)-NH_2$ ($C=O$ (ii)) ($C-N$ (ii))	C_a	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	90.51	89.49	41.30	1.31755	0.00672
$HC_a(NH_2)=O$ ($C=O$ (i))	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$HC_a(NH_2)=O$ ($C=O$ (i))	C'_a	-1.79278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	135.44	44.56	63.28	0.58044	0.55569
$RC_bH_2C_a(NH_2)=O$ ($C=O$ (ii))	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RC_bH_2C_a(NH_2)=O$ ($C=O$ (ii))	C'_a	-1.34946	-0.82688	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	133.67	46.33	61.70	0.61582	0.52395
$H-C'(O)NH_2$ ($C'H$ (i))	C'	-1.79278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	62.39	117.61	32.13	1.41810	0.36148
$RH_2C_b-C_a(O)NH_2$	C_a	-0.92918	-1.34946	-0.82688	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	57.02	122.98	25.76	1.84386	0.41299
$H_3C_b-C_a(O)NH_2$	C_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$RH_2C_cH_2C_b-C_a(O)NH_2$	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$C'-H\left(C'H_3\right)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\left(C'H_2\right)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\left(C'H\right)$ (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC_bH_2C'H_2-$ ($C'-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC_bH_2C'H_2-$ ($C'-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C'-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R''-H_2C_d\right)C_b\left(R''-H_2C_e\right)C'H_2-$ ($C'-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HC'H_2-$ ($C'-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R''-H_2C_d\right)C_b\left(R''-H_2C_e\right)C'H_2-$ ($C'-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HC'H_2-$ ($C'-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R''-H_2C_d\right)C_b\left(R''-H_2C_e\right)C'H_2-$ ($C'-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.114. The energy parameters (eV) of functional groups of alkyl amides.

Parameters	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH_2 Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	2	2	1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
C_1	0.75	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	0.93613	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.85395	0.85395	0.91140	0.91140	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	2	2	0	0	0	0	1	1	0	0	0	1	1	0
c_4	1	2	4	4	2	2	1	1	1	1	2	2	2	2	2	2
c_5	1	0	0	0	0	0	2	3	2	1	0	0	0	0	0	0
C_{1n}	0.75	1	0.5	0.5	0.5	0.5	1.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2n}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_c (eV)	-35.12015	-30.19634	-112.61934	-111.25473	-38.24008	-36.88558	-78.77719	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_e (eV)	12.87680	9.50874	23.95107	23.87467	10.40705	10.27417	28.03446	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	10.48582	7.37432	43.62389	42.82081	11.18655	10.51650	29.77286	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ne} (eV)	-5.24291	-3.68716	-21.81195	-21.41040	-5.59327	-5.25825	-14.88643	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(no\ no)$ (eV)	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14.53414	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(no\ no)$ (eV)	0	0	-3.58557	-2.69893	-5.23932	-4.35268	-1.65376	0	0	0	0	0	0	0	0	0
$E_T(no\ no)$ (eV)	-14.63489	-14.63489	3.58557	2.69893	-9.39557	-10.28221	-12.88038	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E(n_{1s}no\ no)$ (eV)	0	0	0	0	0	0	-14.53414	0	0	0	0	0	0	0	0	0
$E_T(n_2MO)$ (eV)	-31.63533	-31.63534	-63.27075	-63.27074	-31.63533	-31.63537	-48.73668	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	0	-1.85836	-3.58557	-2.69893	-1.65376	-1.65376	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-31.63537	-33.49373	-66.85630	-65.96966	-33.28912	-33.28912	-48.73660	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	24.1759	14.1117	60.9581	59.4034	13.0822	12.5874	59.4067	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	15.91299	9.28860	40.12366	39.10034	8.61093	8.28526	39.10250	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{ji}$ (eV)	-0.24966	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.39136	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kvib}$ (eV)	0.35532 (Eq. (13.458))	0.14655 [28]	0.21747 [32]	0.21077 [12]	0.17358 [33]	0.17358 [33]	0.40929 [22]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{aa}$ (eV)	-0.07200	-0.12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.18672	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{nag} (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-31.70737	-33.62241	-67.47664	-66.57498	-33.39559	-33.39190	-49.11003	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(e_i\ no\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(e_i\ no\ no)$ (eV)	-13.59844	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{ji}(Group)$ (eV)	3.47404	4.35263	8.70826	7.80660	4.12581	4.12212	7.37901	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.115. The total bond energies of alkyl amides calculated using the functional group composition and the energies of Table 15.114 compared to the experimental values [3].

Formula	Name	$C-H$ (i) Group	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH_2 Group	CH_3	CH_2	CH (ii)	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO	Formamide	1	0	1	0	1	0	1	0	0	0	0	0	0	0	0	0	23.68712	23.697	0.00041
C_2H_5NO	Acetamide	0	1	0	1	0	1	1	1	0	0	0	0	0	0	0	0	36.15222	36.103	-0.00135
C_3H_7NO	Propanamide	0	1	0	1	0	1	1	1	1	0	1	0	0	0	0	0	48.30992	48.264	-0.00094
C_4H_9NO	Butanamide	0	1	0	1	0	1	1	1	2	0	2	0	0	0	0	0	60.46762	60.449	-0.00030
C_4H_9NO	2-Methylpropanamide	0	0	0	1	0	1	1	2	0	1	0	3	0	0	0	0	60.51509	60.455	-0.00099
$C_5H_{11}NO$	Pentanamide	0	1	0	1	0	1	1	1	3	0	3	0	0	0	0	0	72.65232	72.481	-0.00200
$C_5H_{11}NO$	2,2-Dimethylpropanamide	0	0	0	1	0	1	1	3	0	0	0	3	0	0	0	0	72.67890	72.718	0.00054
$C_6H_{13}NO$	Hexanamide	0	1	0	1	0	1	1	1	4	0	4	0	0	0	0	0	84.78302	84.780	-0.00004
$C_8H_{17}NO$	Octanamide	0	1	0	1	0	1	1	1	6	0	6	0	0	0	0	0	109.09842	109.071	-0.00025

Table 15.116. The bond angle parameters of alkyl amides and experimental values [1]. In the calculation of θ_0, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_0 (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HNH$	1.94130	1.94130	3.1464	-14.53414	N	H	H	0.93613 Eq. (15.62))	1	1	1	0.75	1.06823	0				108.27	
$\angle C_\alpha NH$ (CH (i); $C_\alpha=O$ (i))	2.61473	1.94130	3.9328	-14.53414 N	N	-14.82575 C_α	1	0.93613 (Eq. (15.62))	0.91771	0.75	1	0.75	0.98033	0				118.61	119.2 (formamide)
$\angle HC_\alpha N$ (CH (i); $C_\alpha=O$ (i))	2.11323	2.61473	4.0825	-14.82575 C_α	1	-14.53414 N	N	0.91771	0.93613 (Eq. (15 62))	0.75	1	0.75	1.02006	0				119.04	
$\angle HC_\alpha O_\sigma$ (CH (i))	2.11323	2.27227	3.7238	-14.82575 C_α	1	-13.61806	O	0.91771	0.85395 (Eq. (15.114))	0.75	1	0.75	0.93052	0				116.18	
$\angle OC_\alpha N$ ($C_\alpha=O$ (i))	2.27227	2.61473	4.3359	16.17521 O	12	-16.37720 N	17	0.84115	0.83078	1	1	1	0.83596	-1.44915				124.91	125.0 (formamide)
$\angle C_\beta C_\alpha N$ ($C_\alpha=O$ (ii))	2.86175	2.64855	4.6904	-15.75493 C_β	7	-14.53414 N	N	0.86359	0.91140 (Eq. (15.116))	1	1	1	0.88749	-1.44915				116.63	115.1 (acetamide)
$\angle C_\beta C_\alpha O$ ($C_\alpha=O$ (ii))	2.86175	2.27954	4.5607	-16.68411	24	-13.61806	O	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				124.63	
$\angle OC_\alpha N$ ($C_\alpha=O$ (ii))	2.27954	2.64855	4.3128	16.17521 O	12	-16.37720 N	17	0.84115	0.83078	1	1	1	0.83596	-1.44915				121.95	122.0 (acetamide)
Methylene $\angle HC_\alpha H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_\alpha C_\beta C_\gamma$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_\alpha C_\beta H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_\alpha H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_\alpha C_\beta C_\gamma$															70.56			109.44	
$\angle C_\alpha C_\beta H$															70.56			109.44	
$\angle C_\beta C_\alpha C_\gamma$ iso C_α	2.91547	2.91547	4.7958	-16.68412 C_β	25	-16.68412 C_β	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_\beta C_\alpha H$ iso C_α	2.91547	2.11323	4.1633	-15.55033 C_α	5	-14.82575 C_β	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_\alpha C_\beta H$ iso C_α	2.91547	2.09711	4.1633	-15.55033 C_β	5	-14.82575 C_α	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_\beta C_\alpha C_\varepsilon$ tert C_α	2.90327	2.90327	4.7958	-15.55033 C_β	5	-14.82575 C_ε	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_\beta C_\alpha C_\delta$															72.50			107.50	

N-ALKYL AND N,N-DIALKYL-AMIDES ($C_nH_{2n+1}NO,\ n=2,3,4,5...\infty$)

The N-alkyl and N,N-dialkyl amides, $C_nH_{2n+1}NO$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. Formamide has a $HC=O$ moiety that comprises a more stable $C=O$ functional group and a CH functional group that is equivalent to that of the iso-CH group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a $C-N(R_1)R_2$ moiety that comprises two types of $C-N$ functional groups, one for formamide and the other for alkyl amides ($RC(O)N(R_1)R_2$ where R is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a single methyl or alkyl substitution, the $NH-C$ bond and NH are functional groups, and the $N-C$ bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The NH functional group was solved in the Hydrogen Nitride (NH) section except that the energy of the $N-H$ MO is matched to the nitrogen-atom contribution to $\Delta E_{H_2MO}(AO/HO)$ and $E_T(atom-atom, msp^3.AO)$ of the $C-N$ group. The $C-C(O)$ group, both N-alkyl or N,N-dialkyl amide $C=O$ groups, and both $C-N$ groups are equivalent to those given in the Amides section.

As in the case of primary amines, each $N-C$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the

$N-C$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the $N-C$-bond MO given by Eq. (15.114) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$.

$E_T\left(atom-atom,msp^3.AO\right)$ of the N-substituted amide $C-C(O)$ group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides, $-1.85836\ eV$, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

$E_T\left(atom-atom,msp^3.AO\right)$ (Eq. (15.52)) of the $C=O$ group of N-substituted alky amides and the $C=O$ group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the Carboxylic Acids section are $-2.69893\ eV$ and $-3.58557\ eV$, respectively.

$E_T\left(atom-atom,msp^3.AO\right)$ of both $C-N$ functional groups are the same as those of the corresponding groups of amides, $-1.65376\ eV$. $E_T\left(atom-atom,msp^3.AO\right)$ of the singly-substituted $NH-C$-bond MO in Eq. (15.52) due to the charge donation from the N and C atoms to the MO is $-0.92918\ eV$. It is equivalent to that of tertiary amines and matches the energy of the $NH-C$ group to that of the $C-N$ group wherein $E_T\left(atom-atom,msp^3.AO\right)$ of the latter is a linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-0.72457\ eV$ (Eq. (14.151)). $E_T\left(atom-atom,msp^3.AO\right)$ of the doubly-substituted $N-C$-bond MO is $-0.72457\ eV$. It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the $N-C$ group to that of the $C-N$ group by matching one of the components of $E_T\left(atom-atom,msp^3.AO\right)$ of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122.

Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

Functional Group	Group Symbol
C-C(O)	$C-C(O)$
C=O (N-alkyl and N,N-dialkyl formamide)	$C=O$ (i)
C=O (N-alkyl and N,N-dialkyl amide)	$C=O$ (ii)
(O)C-N (N-alkyl and N,N-dialkyl formamide)	$C-N$ (i)
(O)C-N (N-alkyl and N,N-dialkyl amide)	$C-N$ (ii)
NH group	NH
N-C (N-alkyl)	$N-C$ (i)
N-C (N,N,-dialkyl)	$N-C$ (ii)
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.118. The geometrical bond parameters of N-alkyl and N,N-dialkyl amides and experimental values [1]

Parameter	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH Group	$N-C$ (i) Group	$N-C$ (ii) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_o)$	2.04740	1.290799	1.29907	1.70920	1.75370	1.28620	1.96313	1.97794	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_o)$	1.43087	1.13613	1.13977	1.30736	1.32427	0.95706	1.40112	1.40639	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (A)$	1.51437	1.20243	1.20628	1.38365	1.40155	1.01291	1.48288	1.48846	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.520 (N-methyl-acetamide)	1.212 (formamide)	1.225 (N-methyl-acetamide)	1.368 (formamide)	1.380 (acetamide)		1.469 (N-methyl-acetamide)		1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_o)$	1.46439	0.61267	0.62331	1.10098	1.14968	0.85927	1.37505	1.39079	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.69887	0.88018	0.87737	0.76490	0.75513	0.74410	0.71372	0.71104	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.119. The MO to HO intercept geometrical bond parameters of N-alkyl and N,N-dialkyl amides. R, R', R'' are H, methyl, or alkyl groups. E_T is $E_T(atom-atom, msp^3\text{-}AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_o)	r_{final} (a_o)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_o)	d_2 (a_o)
$R'C_a(O)N(C_bR)-H$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		115.47	64.53	62.49	0.59403	0.36303
$RC_a(O)N(H)-C_bH_3$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (i)$)$	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		78.61	101.39	37.00	1.56779	0.16667
$RC_a(O)N(H)-C_bH_3$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (i)$)$	C_b	-0.46459	0	0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	83.37	96.63	40.00	1.50383	0.10271
$R'C_a(O)N(H)-C_bH_2C_cH_2R$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (i)$)$	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		78.61	101.39	37.00	1.56779	0.16667
$R'C_a(O)N(H)-C_bH_2C_cH_2R$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (i)$)$	C_b	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21952	-16.02866	78.02	101.39	36.64	1.57525	0.17413
$R'C_a(O)N(C_cH_3)-C_bH_3$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (ii)$)$	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		75.57	104.43	35.35	1.61336	0.20697
$R'C_a(O)N(C_cH_3)-C_bH_3$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (ii)$)$	C_b	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	82.59	97.41	39.70	1.52188	0.11549
$R'C_a(O)N(C_cH_2C_dH_2R)-C_bH_3$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (ii)$)$	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		75.57	104.43	35.35	1.61336	0.20697
$R'C_a(O)N(C_cH_2C_dH_2R)-C_bH_3$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (ii)$)$	C_b	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	82.59	97.41	39.70	1.52188	0.11549
$R''C_a(O)N(R')-C_bH_2C_cH_2R$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (ii)$)$	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		75.57	104.43	35.35	1.61336	0.20697
$R''C_a(O)N(R')-C_bH_2C_cH_2R$ $(C=O$ (i) and (ii)$)$ $(C-N$ (i) and (ii)$)$ $(N-C$ (ii)$)$	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	77.12	102.88	36.28	1.59451	0.18812
$HC_a(O)-N(H)R$ $(C=O$ (i)$)$ $(C-N$ (i)$)$ $(N-C$ (i)$)$ *R = methyl or alkyl*	N	-0.82688	-0.46459	0	0		0.93084	0.84418	-16.11722		102.07	77.93	48.57	1.13090	0.17647
$HC_a(O)-N(H)R$ $(C=O$ (i)$)$ $(C-N$ (i)$)$ $(N-C$ (i)$)$ *R = methyl or alkyl*	C_a	-0.82688	-1.79278	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	96.81	83.19	44.70	1.21492	0.09244
$HC_a(O)-N(R')R$ $(C=O$ (i)$)$ $(C-N$ (i)$)$ $(N-C$ (ii)$)$ *R,R' = methyl or alkyl*	N	-0.82688	-0.36229	-0.36229	0		0.93084	0.83078	-16.37720		101.03	78.97	47.79	1.14842	0.15895
$HC_a(O)-N(R')R$ $(C=O$ (i)$)$ $(C-N$ (i)$)$ $(N-C$ (ii)$)$	C_a	-0.82688	-1.79278	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	96.81	83.19	44.70	1.21492	0.09244

R,R' = methyl or alkyl																
R'H$_2$C$_b$C$_c$(O)–N'(H)R																
(C = O (ii))	N	-0.82688	-0.46459	0	0		0.95084	0.84418	-16.11722		98.16	81.84	46.62	1.20446	0.11982	
(C–N (ii))																
(N–C (i))																
R = methyl or alkyl																
R'H$_2$C$_b$C$_c$(O)–N'(H)R																
(C = O (iii))	C_a	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	90.51	89.49	41.30	1.31755	0.06672	
(C–N (ii))																
(N–C (i))																
R = methyl or alkyl																
R'''H$_2$C$_b$C$_c$(O)–N'(R')R																
(C = O (ii))	N	-0.82688	-0.36229	0			0.95084	0.83078	-16.37720		97.06	82.94	45.82	1.22220	0.10297	
(C–N (ii))																
(N–C (ii))																
R,R' = methyl or alkyl																
R'''H$_2$C$_b$C$_c$(O)–N'(R')R																
(C = O (ii))	C_a	-0.82688	-1.34946	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	90.51	89.49	41.30	1.31755	0.06672	
(C–N (ii))																
(N–C (iii))																
R,R' = methyl or alkyl																
HC$_a$(N'(R'')R')=O																
(C = O (i))	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978	
R',R'' = H, methyl, or alkyl																
HC$_a$(N'(R'')R')=O																
(C = O (i))	C_a	-1.79278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	135.44	44.56	63.28	0.58044	0.55569	
R',R'' = H, methyl, or alkyl																
HC$_a$H$_2$C$_b$C$_c$(N'(R'')R')=O																
(C = O (ii))	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784	
R',R'' = H, methyl, or alkyl																
HC$_a$H$_2$C$_b$C$_c$(N'(R'')R')=O																
(C = O (ii))	C_a	-1.34946	-0.82688	-0.92918	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	133.67	46.33	61.70	0.61582	0.52395	
R',R'' = H, methyl, or alkyl																
H–C'(O)N'(R'')R'																
R',R'' = H, methyl, or alkyl	C'	-1.79278	-0.82688	0	0	-154.23535	0.91771	0.77991	-17.44541	-17.25455	62.39	117.61	32.13	1.41810	0.36148	
RH$_2$C$_b$–C$_c$(O)N'(R'')R'																
R',R'' = H, methyl, or alkyl	C_a	-0.92918	-1.34946	-0.82688	0	-154.72121	0.91771	0.75878	-17.93127	-17.74041	57.02	122.98	25.76	1.84386	0.41259	
H$_3$C$_b$–C$_c$(O)N'(R'')R'																
R',R'' = H, methyl, or alkyl	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301	
RH$_2$C$_b$H$_2$C$_b$–C$_c$(O)N'(R'')R'																
R',R'' = H, methyl, or alkyl	C_a	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183	
C'–H (CH$_3$)	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708	
C'–H (CH$_2$)	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933	
C'–H (CH) (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37336	
H$_3$C$_a$C$_b$H$_2$CH$_2$–																
(C'–C (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	65.82	116.18	30.08	1.83879	0.38106	
H$_3$C$_a$C$_b$H$_2$CH$_2$–																
(C'–C (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117	
R–H$_2$C$_a$C$_b$(H$_2$C$_a$ – R')HC'H$_2$–																
(C'–C (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388	
R–H$_2$C$_a$C$_b$(R'–H$_2$C$_a$)C$_b$(R''–H$_2$C$_a$)C'H$_2$–																
(C'–C (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71869	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570	
isoC$_a$H$_2$C$_b$(H$_2$C$_a$ – R')HC'H$_2$–																
(C'–C (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388	
neoC$_a$(R''–H$_2$C$_a$)C$_b$(R''–H$_2$C$_a$)CH$_2$–																
(C'–C (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298	
neoC$_a$H$_2$C$_b$(H$_2$C$_a$ – R')HC'H$_2$–																
(C'–C (f))	C_b	-0.72457	-0.92918	-0.92918	-0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279	
isoC$_a$(R''–H$_2$C$_a$)C$_b$(R''–H$_2$C$_a$)C'H$_2$–																
(C'–C (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298	

Table 15.120. The energy parameters (eV) of functional groups of N-alkyl and N,N-dialkyl amides.

Parameters	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH Group	$N-C$ (i)	$N-C$ (ii)	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	2	1	1	1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	0.93613	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	0.75	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.85395	0.85395	0.91140	0.91140	1	0.91140	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	2	2	0	0	1	0	0	0	1	1	0	0	0	1	1	0
c_4	2	4	4	2	2	1	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	0	0	1	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	1	0.5	0.5	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-30.19634	-112.61934	-111.25473	-38.24008	-36.88558	-40.92593	-31.67393	-31.36351	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_n (eV)	9.50874	23.95107	23.87467	10.40705	10.27417	14.21618	9.71067	9.67426	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.37432	43.62389	42.82081	11.18655	10.51650	15.90963	8.06719	7.92833	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{es} (eV)	-3.68716	-21.81195	-21.41040	-5.59327	-5.25825	-7.95482	-4.03359	-3.96416	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(no\ no)$ (eV)	-14.63489	0	0	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H\text{-}BD}(no\ no)$ (eV)	0	-3.58557	-2.69893	-5.23932	-4.35268	-1.65376	-0.92918	-0.72457	0	0	0	0	0	0	0	0	0
$E_p(no\ no)$ (eV)	-14.63489	3.58557	2.69893	-9.39557	-10.28221	-12.88038	-13.70571	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{\pi}(\pi_{2sp2})$ (eV)	-31.63534	-63.27075	-63.27074	-31.63533	-31.63537	-31.63531	-31.63537	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{\pi}(atom-atom, msp^2.AO)$ (eV)	-1.85836	-3.58557	-2.69893	-1.65376	-1.65376	0	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{\pi}(no)$ (eV)	-33.49373	-66.85630	-65.96966	-33.28912	-33.28912	-31.63537	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{14}\ rad/s)$	14.1117	60.9581	59.4034	13.0822	12.5874	44.9494	10.6278	10.5087	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_{ss} (eV)	9.28860	40.12366	39.10034	8.61093	8.28526	29.58649	6.99543	6.91703	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_{ep}$ (eV)	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.34043	-0.17039	-0.16837	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Keb}$ (eV)	0.14655 [28]	0.21747 [32]	0.21077 [12]	0.17358 [33]	0.17358 [33]	0.40696 [24]	0.12944 [23]	0.12944 [23]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{coc}$ (eV)	-0.12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.13695	-0.10567	-0.10365	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{ang} (eV)	0.14803	0.11441	0.11441	0.14803	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\pi}(\pi_{2sp2})$ (eV)	-33.62241	-67.47664	-66.57498	-33.39559	-33.39190	-31.77232	-32.67022	-32.46359	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{emb,d}(e_s, no\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{emb,d}(e_s, no\ no)$ (eV)	0	0	0	0	0	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\pi}(\pi_{2sp2})$ (eV)	4.35263	8.70826	7.80660	4.12581	4.12212	3.49788	3.40044	3.19381	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.121. The total bond energies of N-alkyl and N,N-dialkyl amides calculated using the functional group composition and the energies of Table 15.120 compared to the experimental values [3].

Formula	Name	$C-C(O)$ Group	$C=O$ (i) Group	$C=O$ (ii) Group	$C-N$ (i) Group	$C-N$ (ii) Group	NH Group	$N-C$ (i)	$N-C$ (ii)	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_3H_7NO	N,N-Dimethylformamide	0	1	0	1	0	0	0	2	2	0	1	0	0	0	0	0	0	47.53142	47.574	0.00090
C_4H_9NO	N,N-Dimethylacetamide	0	0	1	0	2	0	0	2	3	0	0	0	0	0	0	0	0	59.91404	59.890	-0.00041
$C_6H_{13}NO$	N-Butylacetamide	1	0	1	0	1	1	1	0	2	3	0	3	0	0	0	0	0	84.63649	84.590	-0.00055

Table 15.122. The bond angle parameters of N-alkyl and N,N-dialkyl amides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_n)	$2c'$ Bond 2 (a_n)	$2c'$ Terminal Atoms (a_n)	$E'_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E'_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_1 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle OC_aN$ ($C_a=O$ (ii))	2.27954	2.64855	4.3243	16.17521 O	12	-16.11722 N	11	0.84115	0.84418	1	1	1	0.84266	-1.44915				122.51	121.8 (N-methylacetamide)
$\angle C_bC_aN$ ($C_a=O$ (ii))	2.86175	2.64855	4.6904	-15.75493 C_b	7	-14.53414 N	N	0.86359	0.91140 (Eq. (15.116))	1	1	1	0.88749	-1.44915				116.63	114.1 (N-methylacetamide)
$\angle C_bC_aO$ ($C_a=O$ (ii))	2.86175	2.27954	4.5607	-16.68411	24	-13.61806	O	0.81549	0.85395 (Eq. (15.114))	1	1	1	0.83472	-1.65376				124.63	
$\angle C_aNC_c$ ($C_a=O$ (ii))	2.64855	2.80224	4.6904	-17.93127 C_a	48	-16.21952 C_c	14	0.75878	0.83885	1	1	1	0.79881	-1.85836				118.72	119.7 (N-methylacetamide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

UREA (CH_4N_2O)

Urea, CH_4N_2O, comprises a $C=O$ functional group and two $C-NH_2$ moieties that each comprise a NH_2 functional group and a $C-N$ functional group. The $C=O$ group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The NH_2 and $C-N$ functional groups are also equivalent to those given in the Amides section. $E_T\left(atom-atom,msp^3.AO\right)$ (Eq. (15.52)) of the $C=O$ and $C-N$ groups are equivalent to those of formamide. The values given in the Amides section are $-3.58557\ eV$, and $-1.65376\ eV$, respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.79-15.108) are given in Table 15.128.

Table 15.123. The symbols of functional groups of urea.

Functional Group	Group Symbol
C=O (urea)	$C=O$
(O)C-N (urea)	$C-N$
NH_2 group	NH_2

Table 15.124. The geometrical bond parameters of urea and experimental values [1].

Parameter	$C=O$ Group	$C-N$ Group	NH_2 Group
$a\ (a_0)$	1.290799	1.70920	1.32297
$c'\ (a_0)$	1.13613	1.30736	0.97065
Bond Length $2c'\ (A)$	1.20243	1.38365	1.02729
Exp. Bond Length (A)	1.212 (formamide)	1.368 (formamide)	1.027 (formamide) 1.022 (acetamide)
$b,c\ (a_0)$	0.61267	1.10098	0.89894
e	0.88018	0.76490	0.75369

Table 15.125. The MO to HO intercept geometrical bond parameters of urea. E_T is $E_T(atom-atom, nsp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_2NC(O)N(H)-H$	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		113.90	66.10	62.13	0.61843	0.35222
$H_2NC(O)-NH_2$	N	-0.82688	0	0	0		0.93084	0.86923	-15.65263		103.93	76.07	50.02	1.09814	0.20922
$H_2NC(O)-NH_2$	C'	-0.82688	-1.79278	-0.82688	0	-155.06223	0.91771	0.74461	-18.27229	-18.08143	93.56	86.44	42.45	1.26106	0.04630
$H_2NC_a(NH_2)=O$	O	-1.79278	0	0	0		1.00000	0.81871	-16.61853		137.10	42.90	65.45	0.53635	0.59978
$H_2NC_a(NH_2)=O$	C'	-1.79278	-0.82688	-0.82688	0	-155.06223	0.91771	0.74461	-18.27229	-18.08143	133.82	46.18	61.27	0.62054	0.51559

Table 15.126. The energy parameters (eV) of functional groups of urea.

Parameters	$C=O$ Group	$C-N$ Group	NH_2 Group
n_1	2	1	2
n_2	0	0	0
n_3	0	0	1
C_1	0.5	0.5	0.75
C_2	1	1	0.93613
c_1	1	1	0.75
c_2	0.85395	0.91140	1
c_3	2	0	0
c_4	4	2	1
c_5	0	0	2
$C_{1\omega}$	0.5	0.5	1.5
$C_{2\omega}$	1	1	1
$V_e\ (eV)$	-112.61934	-38.24008	-78.77719
$V_p\ (eV)$	23.95107	10.40705	28.03446
$T\ (eV)$	43.62389	11.18655	29.77286
$V_m\ (eV)$	-21.81195	-5.59327	-14.88643
$E(AO/HO)\ (eV)$	0	-14.63489	-14.53414
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	-3.58557	-5.23932	-1.65376
$E_T(AO/HO)\ (eV)$	3.58557	-9.39557	-12.88038
$E(n_3\ AO/HO)\ (eV)$	0	0	-14.53414
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63533	-48.73668
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-3.58557	-1.65376	0
$E_T(MO)\ (eV)$	-66.85630	-33.28912	-48.73660
$\omega\ \left(10^{15}\ rad/s\right)$	19.9334	13.0822	59.4067
$E_K\ (eV)$	13.12053	8.61093	39.10250
$\bar{E}_D\ (eV)$	-0.23955	-0.19325	-0.39136
$\bar{E}_{Kvib}\ (eV)$	0.21747 [32]	0.17358 [33]	0.40929 [22]
$\bar{E}_{osc}\ (eV)$	-0.13081	-0.10647	-0.18672
$E_{mag}\ (eV)$	0.11441	0.14803	0.14185
$E_T(Group)\ (eV)$	-67.11793	-33.39559	-49.11003
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.53414
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	0	-13.59844
$E_D(Group)\ (eV)$	8.34955	4.12581	7.37901

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

Formula	Name	$C=O$ Group	$C-N$ Group	NH_2 Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_4N_2O	Urea	1	2	2	31.35919	31.393	0.00108

Table 15.128. The bond angle parameters of urea and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3,AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E'_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E'_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HNH$	1.94130	1.94130	3.1464	-14.53414	N	H	H	0.93613 Eq. (15.62))	1	1	1	0.75	1.06823	0				108.27	
$\angle C'_nNH$	2.61473	1.94130	3.9328	-14.53414 N	N	-14.82575 C'_n	1	0.93613 (Eq. (15.62))	0.91771	0.75	1	0.75	0.98033	0				118.61	119.2 (formamide)
$\angle OC'_nN$	2.27227	2.61473	4.3359	16.17521 O	12	-16.37720 N	17	0.84115	0.83078	1	1	1	0.83596	-1.44915				124.91	125.0 (formamide)

CARBOXYLIC ACID HALIDES ($C_nH_{2n-1}OX,\ X=F,Cl,Br,I;\ n=1,2,3,4,5...\infty$)

The alkyl carboxylic acid halides, $C_nH_{2n-1}OX$, comprise a $C=O$ functional group, and the single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. All carboxylic acid halides further comprise a $C-X$ functional group where X is a halogen atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide $C=O$ and $C-C(O)$ groups are equivalent to those given in the Aldehydes section and the Ketones section, respectively. The values of $E_T\left(atom-atom,msp^3.AO\right)$ given in these sections are $-2.69893\,eV$ and $-1.44915\,eV$, respectively.

As in the case of alkyl halides, each $(O)C-X$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the $(O)C-Cl$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor C_2 of Eq. (15.52) for the $(O)C-Cl$-bond MO given by Eq. (15.111) is $C_2\left(C2sp^3HO\ to\ Cl\right)=0.81317$. The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the $C-Cl$ group of alkyl chlorides, $E_T\left(atom-atom,msp^3.AO\right)$ of the $(O)C-Cl$-bond MO in Eq. (15.52) of alky carboxylic acid chlorides due to the charge donation from the C and Cl atoms to the MO is $-1.44915\,eV$ where both energy contributions

are given by Eq. (14.511). This matches the energy of the $C-C(O)$ functional group with that of the $(O)C-Cl$ group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs. (15.79-15.108) are given in Table 15.134.

Table 15.129. The symbols of functional groups of alkyl carboxylic acid chlorides.

Functional Group	Group Symbol
C-C(O)	$C-C(O)$
C=O (alkyl carboxylic acid chloride)	$C=O$
(O)C-Cl	$C-Cl$
CH_3 group	$C-H\left(CH_3\right)$
CH_2 group	$C-H\left(CH_2\right)$
CH (alkyl) group	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.130. The geometrical bond parameters of alkyl carboxylic acid chlorides and experimental values [1].

Parameter	$C-C(O)$ Group	$C=O$ Group	$C-Cl$ Group	$C-H\left(CH_3\right)$ Group	$C-H\left(CH_2\right)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\left(a_0\right)$	2.04740	1.29907	2.32621	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\left(a_0\right)$	1.43087	1.13977	1.69136	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\left(A\right)$	1.51437	1.20628	1.79005	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $\left(A\right)$	1.520 (acetone) 1.518 (2-butanone)	1.187 (acetyl chloride) 1.214 (acetic acid)	1.798 (acetyl chloride)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\left(a_0\right)$	1.46439	0.62331	1.59705	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.69887	0.87737	0.72709	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides. R,R',R'' are H or alkyl groups. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_3C_bC_a(O)-Cl$	Cl	-0.72457	0	0	0		1.05158	0.87495	-15.55033		69.62	110.38	30.90	1.99599	0.30463
$H_3C_bC_a(O)-Cl$	C_a	-1.34946	-0.72457	-0.72457	0	-154.41430	0.91771	0.77199	-17.62436	-17.43350	54.69	125.31	23.23	2.13760	0.44625
$H_3C_bC_a(Cl)=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$H_3C_bC_a(Cl)=O$	C_a	-1.34946	-0.72457	-0.72457	0	-154.41430	0.91771	0.77199	-17.62436	-17.43350	134.28	45.72	62.45	0.60076	0.53901
$H_3C_b-C_a(O)-Cl$	C_a	-0.72457	-1.34946	-0.72457	0	-154.41430	0.91771	0.77199	-17.62436	-17.43350	59.30	120.70	26.96	1.82495	0.39408
$H_3C_b-C_a(O)-Cl$	C_b	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	73.62	106.38	34.98	1.67762	0.24675
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$ (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_c)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.132. The energy parameters (eV) of functional groups of alkyl carboxylic acid chlorides.

Parameters	$C-C(O)$ Group	$C=O$ Group	$C-Cl$ Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	0.81317	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.85395	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	2	1	0	1	1	0	0	0	1	1	0
c_4	2	4	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	0.81317	1	1	1	1	1	1	1	1	1
V_e (eV)	-30.19634	-111.25473	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_n (eV)	9.50874	23.87467	8.04432	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.37432	42.82081	6.38036	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ee} (eV)	-3.68716	-21.41040	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO\ nn)$ (eV)	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(AO\ nn)$ (eV)	0	-2.69893	-1.44915	0	0	0	0	0	0	0	0	0
$E_p(AO\ nn)$ (eV)	-14.63489	2.69893	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_1(n_1MO)$ (eV)	-31.63534	-63.27074	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{rr}(atom-atom, msp^3.AO)$ (eV)	-1.44915	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_r(MO)$ (eV)	-33.08452	-65.96966	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	16.4962	59.4034	7.42995	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	10.85807	39.10034	4.89052	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_{ij}$ (eV)	-0.21568	-0.40804	-0.14475	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kab}$ (eV)	0.14655 [28]	0.21077 [12]	0.09063 [34]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{exc}$ (eV)	-0.14240	-0.30266	-0.09943	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{nuc} (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-33.22692	-66.57498	-33.18395	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(c_i.AO\ nn)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_i.AO\ nn)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{fg}(Group)$ (eV)	3.95714	7.80660	3.76614	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.133. The total bond energies of alkyl carboxylic acid chlorides calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3].

Formula	Name	$C-C(O)$ Group	$C=O$ Group	$C-Cl$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3ClO	Acetyl chloride	1	1	1	1	0	0	0	0	0	0	0	0	28.02174	27.990	-0.00115

Table 15.134. The bond angle parameters of alkyl carboxylic acid chlorides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (u_0)	$2c'$ Bond 2 (u_n)	$2c'$ Terminal Atoms (u_n)	$E_{Conjugate}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Conjugate}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_bC_aO$	2.86175	2.27954	4.5826	-16.68411	24	-13.61806	O	0.81549	0.85395 (Eq. (15.113))	1	1	1	0.83472	-1.65376				125.70	
$\angle C_bC_aCl$	2.86175	3.38271	5.1539	-15.75493 C_b	7	-12.96764 Cl	Cl	0.86359	0.86359	1	0.81317 (Eq. (15.111))	1	0.86359	-0.92918				110.98	111.6 (acetyl chloride)
$\angle OC_aCl$	2.27954	3.38271	4.9841	-16.68412 O	25	-15.55033 Cl	5	0.81549	0.87495	1	0.81317 (Eq. (15.111))	1	0.84522	-0.92918				122.13	121.2 (acetyl chloride)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.6 (acetyl chloride) 108.5 (acetone)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

CARBOXYLIC ACID ANHYDRIDES ($C_nH_{2n-2}O_3$, $n = 2,3,4,5...\infty$)

The alkyl carboxylic acid anhydrides, $C_nH_{2n-2}O_3$, have two $(O)C-O$ moieties that each comprise $C=O$ and $C-O$ functional groups. The single bond of carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. The alkyl portion of the alkyl carboxylic acid anhydride may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride $C=O$ and $C-C(O)$ groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of $E_T\left(atom-atom,msp^3.AO\right)$ given in these sections are $-2.69893\,eV$ and $-1.44915\,eV$, respectively. The $C-O$ group is also equivalent to that given in the Carboxylic Acid Esters section except that $E_T\left(atom-atom,msp^3.AO\right)$ is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the $C-O$ group, $E_T\left(atom-atom,msp^3.AO\right)$ is $-1.65376\,eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of each $C-C(O)$ group and is given by the linear combination of $-0.72457\,eV$ (Eq. (14.151)) and $-0.92918\,eV$ (Eq. (14.513)), respectively. This matches $-0.72457\,eV$, the energy contribution of each of the $C2sp^3$ HOs to each $C-C(O)$ functional group, with that of the corresponding energy component of the $C-O$ group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl

carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.79-15.108) are given in Table 15.140.

Table 15.135. The symbols of functional groups of alkyl carboxylic acid anhydrides.

Functional Group	Group Symbol
C-C(O)	$C-C(O)$
C=O (alkyl carboxylic acid anhydride)	$C=O$
(O)C-O	$C-O$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.136. The geometrical bond parameters of alkyl carboxylic acid anhydrides and experimental values [1].

Parameter	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	2.04740	1.29907	1.73490	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.43087	1.13977	1.31716	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.51437	1.20628	1.39402	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.520 (acetone) 1.518 (2-butanone)	1.214 (acetic acid)	1.393 (avg. methyl formate)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h, c\ (a_0)$	1.46439	0.62331	1.12915	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.69887	0.87737	0.75921	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.137. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RC_bH_2C_a(O)-O_a-C_a(O)C_cH_2R'$	O_a	-0.82688	-0.82688	0	0		1.00000	0.82562	-16.47951		98.32	81.68	46.34	1.19766	0.11949
$RC_bH_2C_a(O)-O_a-C_a(O)C_cH_2R'$	C'_a	-0.82688	-1.34946	-0.82688	0	-154.51660	0.91771	0.76753	-17.72667	-17.53580	93.21	86.79	42.74	1.27417	0.04298
$RC_bH_2\left(R'C_cH_2C_a(O_a)O\right)C_a=O_a$	O_a	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$RC_bH_2\left(R'C_cH_2C_a(O_a)O\right)C_a=O_a$	C'_a	-1.34946	-0.72457	-0.82688	0	-154.51660	0.91771	0.76753	-17.72667	-17.53580	134.08	45.92	62.20	0.60583	0.53394
$RH_2C_b-C_a(O)OC_a(O)C_cH_2R'$	C_a	-0.72457	-1.34946	-0.82688	0	-154.51660	0.91771	0.76753	-17.72667	-17.53580	58.55	121.45	26.56	1.83133	0.40045
$H_3C_b-C_a(O)OC_a(O)C_cH_2R'$	C_b	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	73.62	106.38	34.98	1.67762	0.24675
$RH_2C_b-C_a(O)OC_a(O)C_cH_2R'$ $R=alkyl$	C'_b	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	67.40	112.60	31.36	1.74821	0.31734
$C'-H\ \left(C'H_3\right)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ \left(C'H_2\right)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ \left(C'H\right)$ (ii)	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2C'H_2-$ $(C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2C'H_2-$ $(C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0-	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ $(C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$iso(C'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tert(C'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ $(C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tert(C'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$iso(C'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.138. The energy parameters (eV) of functional groups of alkyl carboxylic acid anhydrides.

Parameters	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	CH_3 Group	CH_2 Group	$C-H$ (ii) Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.85395	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	2	0	0	1	1	0	0	0	1	1	0
c_4	2	4	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1a}	1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2a}	1	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-30.19634	-111.25473	-35.08488	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	9.50874	23.87467	10.32968	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.37432	42.82081	10.11150	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ne} (eV)	-3.68716	-21.41040	-5.05575	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(xc\ no\ nn)$ (eV)	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2NO}(xc\ no\ nn)$ (eV)	0	-2.69893	-2.69893	0	0	0	0	0	0	0	0	0
$E_T(xc\ no\ nn)$ (eV)	-14.63489	2.69893	-11.93596	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2NO)$ (eV)	-31.63534	-63.27074	-31.63541	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-1.44915	-2.69893	-1.65376	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(xc)$ (eV)	-33.08452	-65.96966	-33.28912	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ (10^{15}\ rad/s)$	16.4962	59.4034	24.3637	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	10.85807	39.10034	16.03660	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_H$ (eV)	-0.21568	-0.40804	-0.26373	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.14655 [28]	0.21077 [12]	0.13638 [35]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{anc}$ (eV)	-0.14240	-0.30266	-0.19554	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{stage} (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-33.22692	-66.57498	-33.48466	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(e_1.xc\ no\ nn)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(e_2.xc\ no\ nn)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_H(Group)$ (eV)	3.95714	7.80660	4.21488	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.139. The total bond energies of alkyl carboxylic acid anhydrides calculated using the functional group composition and the energies of Table 15.138 compared to the experimental values [3].

Formula	Name	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_6O_3$	Acetic anhydride	2	2	2	2	0	0	0	0	0	0	0	0	56.94096	56.948	0.00013
$C_6H_{10}O_3$	Propanoic anhydride	2	2	2	2	2	0	2	0	0	0	0	0	81.25636	81.401	0.00177

Table 15.140. The bond angle parameters of alkyl carboxylic acid anhydrides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom,msp^3.AO)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle O_a C'_a O_b$	2.27954	2.63431	4.3012	-16.17521 O_a	12	-16.47951 O_b	21	0.84115	0.82562	1	1	1	0.83339	-1.44915				122.00	121.7 [36] (acetic anhydride)
$\angle C'_a O_b C'_a$	2.63431	2.63431	4.4944	-17.30638 C'_b	36	-17.30638 C'_a	36	0.78617	0.78617	1	1	1	0.78617	-1.85836				117.09	115.8 [36] (acetic anhydride)
$\angle C'_b C'_a O_b$	2.86175	2.63431	4.4944	-15.55033	5	-13.61806	O	0.87495	0.85395 (Eq. (15.114))	1	1	1	0.86445	-1.44915				109.65	108.3 [36] (acetic anhydride)
$\angle C'_b C'_a O_a$	2.86175	2.27954	4.6368	-16.47951	21	-13.61806	O	0.82562	0.85395 (Eq. (15.114))	1	1	1	0.83979	-1.65376				128.46	
Methylene $\angle HC'_a H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C'_a C'_b C'_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C'_a C'_b H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC'_a H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	108.6 (acetyl chloride) 108.5 (acetone)
$\angle C'_a C'_b C'_c$															70.56			109.44	
$\angle C'_a C'_b H$															70.56			109.44	
$\angle C'_b C'_a C'_c$ iso C'_a	2.91547	2.91547	4.7958	-16.68412 C'_b	25	-16.68412 C'_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C'_b C'_a H$ iso C'_a	2.91547	2.11323	4.1633	-15.55033 C'_a	5	-14.82575 C'_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C'_a C'_b H$ iso C'_a	2.91547	2.09711	4.1633	-15.55033 C'_b	5	-14.82575 C'_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C'_b C'_a C'_c$ tert C'_a	2.90327	2.90327	4.7958	-15.55033 C'_b	5	-14.82575 C'_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C'_b C'_a C'_d$															72.50			107.50	

NITRILES ($C_nH_{2n-1}N$, $n=2,3,4,5...\infty$)

The nitriles, $C_nH_{2n-1}N$, comprise a $C\equiv N$ functional group, and the single bond of carbon to the nitrile carbon atom, $C-CN$, is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile $C\equiv N$ is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for $\Delta E_{H_2MO}(AO/HO)$ is two times that given in Eq. (14.343), 16.20002 eV, in order to match the N AOs to that of the nitrile $C2sp^3$ HO having a bond order of three. $E_T\left(atom-atom,msp^3.AO\right)$ of the $C\equiv N$ functional group is $-1.56513\,eV$ (Eq. (14.342)) corresponding to the third-order bonded $C2sp^3$ HO.

The $C-CN$ functional group is equivalent to that of an alkyl $C-C$ group given in the Continuous-Chain Alkanes section except that $E_T(H_2MO)$ and $\overline{E}_{Kvib}$ are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section, $E_T\left(atom-atom,msp^3.AO\right)$ of the alkyl $C-C$ group is $-1.85836\,eV$ where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded $C2sp^3$ HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the

$E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of nitriles determined using Eqs. (15.79-15.108) are given in Table 15.146. The C of the $C \equiv N$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes.

Table 15.141. The symbols of functional groups of nitriles.

Functional Group	Group Symbol
C-CN	$C-C$ (i)
CN	$C \equiv N$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH (alkyl) group	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.142. The geometrical bond parameters of nitriles and experimental values [1].

Parameter	$C-C$ (i) Group	$C \equiv N$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.91255	1.20590	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.38295	1.09813	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.46365	1.16221	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.468 (acetonitrile)	1.159 (acetonitrile)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b, c\ (a_0)$	1.382110	0.49828	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
v	0.72309	0.91064	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.143. The MO to HO intercept geometrical bond parameters of nitriles. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RH_2C_bC_a\equiv N$	N	-0.78257	0	0	0		0.93084	0.87170	-15.60832		147.01	32.99	72.28	0.36699	0.73114
$RH_2C_bC_a\equiv N$	C_a	-0.78257	-0.92918	0	0	-153.32744	0.91771	0.82272	-16.53750	-16.34664	145.42	34.58	69.58	0.42077	0.67736
$RH_2C_b-C_aN$	C_a	-0.92918	-0.78257	0	0	-153.32744	0.91771	0.82272	-16.53750	-16.34664	81.32	98.68	38.00	1.50718	0.12423
$H_3C_b-C_aN$	C_b	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	85.50	94.50	40.67	1.45066	0.06771
$RH_2C_cH_2C_b-C_aN$ $R=alkyl$	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	80.53	99.47	37.51	1.51718	0.13423
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$ (ii)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.144. The energy parameters (eV) of functional groups of nitriles.

Parameters	$C-C$ (i) Group	$C \equiv N$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	3	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	1	0	1	1	0	0	0	1	1	0
c_4	2	6	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1a}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2a}	1	1	1	1	1	1	1	1	1	1	1
V_s (eV)	-33.01231	-207.49229	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	9.83824	37.16984	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	8.63043	86.03250	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-4.31522	-43.01625	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(sp^3\text{-}hy)$ (eV)	-14.63489	32.40004	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(sp^3\text{-}hy)$ (eV)	-1.85837	0	0	0	0	0	0	0	0	0	0
$E_T(sp^3\text{-}hy)$ (eV)	-12.77652	32.40004	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2MO)$ (eV)	-31.63537	-94.90616	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	-1.85836	-1.56513	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-33.49374	-96.47124	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	19.2516	22.0753	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	12.67172	14.53031	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D$ (eV)	-0.23588	-0.24250	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kvib}$ (eV)	0.11407 [37]	0.28107 [37]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{one}$ (eV)	-0.17884	-0.10197	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{image} (eV)	0.14803	0.14185	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-33.67258	-96.77713	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(s,sp^3\text{-}hy)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(s,MO)$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	4.40280	8.82594	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.145. The total bond energies of nitriles calculated using the functional group composition and the energies of Table 15.144 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(\text{Group})$ (eV) values based on composition is given by (15.58).

Formula	Name	C–C (i) Group	C≡N Group	CH_3	CH_2	CH	C–C (a)	C–C (b)	C–C (c)	C–C (d)	C–C (e)	C–C (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_3N	Acetonitrile	1	1	1	0	0	0	0	0	0	0	0	0	25.72060	25.77	0.00174
C_3H_5N	Propanenitrile	1	1	1	1	0	1	0	0	0	0	0	0	37.87830	37.94	0.00171
C_4H_7N	Butanenitrile	1	1	1	2	0	2	0	0	0	0	0	0	50.03600	50.08	0.00082
C_4H_7N	2-Methylpropanenitrile	1	1	2	0	1	0	2	0	0	0	0	0	50.13689	50.18	0.00092
C_5H_9N	Pentanenitrile	1	1	1	3	0	3	0	0	0	0	0	0	62.19370	62.26	0.00111
C_5H_9N	2,2-Dimethylpropanenitrile	1	1	3	0	0	0	0	3	0	0	0	-1	62.47823	62.40	-0.00132
$C_7H_{13}N$	Heptanenitrile	1	1	1	5	0	5	0	0	0	0	0	0	86.50910	86.59	0.00089
$C_8H_{15}N$	Octanenitrile	1	1	1	6	0	6	0	0	0	0	0	0	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	1	1	1	8	0	8	0	0	0	0	0	0	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	1	1	1	12	0	12	0	0	0	0	0	0	171.61300	171.70	0.00052

5 Table 15.146. The bond angle parameters of nitriles and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_bC_aN$																			
$\angle HC_bH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				180	
$\angle HC_bC_a$																		109.50	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0	70.56			109.44	109.7 (acetonitrile)
$\angle C_aC_bC_c$																		108.44	107 (propane)
$\angle C_aC_bH$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0	69.51			110.49	111.0 (butane) 111.4 (isobutane)
$\angle C_aC_bC_c$																		109.50	108.5 (acetone)
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836	70.56			109.44	
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.67	110.8 (isobutane)
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

THIOLS ($C_nH_{2n+2}S_m$, $n=1,2,3,4,5...\infty$)

The alkyl thiols, $C_nH_{2n+2}S_m$, comprise a SH functional group and a $C-S$ functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the SH functional group is solved using Eq. (15.41). As in the case of the $C-H$ bonds of CH_n $n=1,2,3$, the $S-H$-bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the $S3p$ shell. The energy of the H_2-type ellipsoidal MO is matched to that of the $S3p$ shell and comprises 75% of a H_2-type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of S, $E(S)=-10.36001\ eV$, is less that that of H, the linear combination of the H_2-type ellipsoidal MO with the $S3p$ shell further comprises an excess 50% charge-density donation from H to the $S3p$ shell of the $S-H$-bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four $3p$ electrons. From Eq. (15.12), the sum $E_T(S,3p)$ of the energies of S, S^+, S^{2+}, and S^{3+} [38] is

$$\begin{aligned} E_T(S,3p) &= 10.36001\ eV + 23.33788\ eV + 34.79\ eV + 47.222\ eV \\ &= 115.70989\ eV \end{aligned} \tag{15.118}$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius r_{3p} of the $S3p$ shell may be calculated from the Coulombic energy using Eqs. (15.13) and (15.118):

$$r_{3p} = \sum_{q=12}^{15} \frac{(Z-q)e^2}{8\pi\varepsilon_0\left(e115.70989\ eV\right)} = \frac{10e^2}{8\pi\varepsilon_0\left(e115.70989\ eV\right)} = 1.17585a_0 \tag{15.119}$$

where $Z=16$ for sulfur. Using Eqs. (15.14) and (15.119), the Coulombic energy $E_{Coulomb}(S,3p)$ of the outer electron of the $S3p$ shell is

$$E_{Coulomb}(S,3p)=\frac{-e^2}{8\pi\varepsilon_0 r_{3p}}=\frac{-e^2}{8\pi\varepsilon_0 1.17585a_0}=-11.57099\ eV \tag{15.120}$$

The sharing of the electrons between the S and H atoms permits the formation an $S-H$-bond MO that is lowered more in energy than the participating $S3p$ orbital which consequently increases in energy. By considering the 50% electron redistribution in the $S-H$ group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius r_{S-H3p} of the $S3p$ shell may be calculated from the Coulombic energy using Eq. (15.18)

$$\begin{aligned} r_{S-H3p} &= \left(\sum_{n=12}^{15}(Z-n)+0.25\right)\frac{e^2}{8\pi\varepsilon_0\left(e115.70989\ eV\right)} \\ &= \frac{10.5e^2}{8\pi\varepsilon_0\left(e115.70989\ eV\right)} \\ &= 1.23465a_0 \end{aligned} \tag{15.121}$$

where the $s=-1$ in Eq. (15.18) due to the charge donation from H to S. Using Eqs. (15.19) and (15.121), the Coulombic energy $E_{Coulomb}\left(S_{S-H},3p\right)$ of the outer electron of the $S3p$ shell is

$$\begin{aligned} E_{Coulomb}\left(S_{S-H},3p\right) &= \frac{-e^2}{8\pi\varepsilon_0 r_{S-H3p}} \\ &= \frac{-e^2}{8\pi\varepsilon_0 1.23465a_0} \\ &= -11.01999\ eV \end{aligned} \tag{15.122}$$

Thus, $E_T\left(S-H,3p\right)$, the energy change of each $S3p$ shell with the formation of the $S-H$-bond MO is given by the difference between Eq. (15.120) and Eq. (15.122):

$$\begin{aligned} E_T\left(S-H,3p\right) &= E\left(S_{S-H},3p\right)-E\left(S,3p\right) \\ &= -11.01999\ eV-\left(-11.57099\ eV\right) \\ &= 0.55100\ eV \end{aligned} \tag{15.123}$$

Then, in Eq. (15.42):

$$\begin{aligned} E_T\left(AO/HO\right) &= E\left(S\right)-E_T\left(S-H,3p\right) \\ &= -10.36001\ eV-0.55100\ eV \\ &= -10.91101\ eV \end{aligned} \tag{15.124}$$

And, in Eq. (15.56),

$$E_T\left(atom-atom,msp^3.AO\right)=0.55100\ eV \tag{15.125}$$

Due to the charge donation from H to S, $c_1 = 1$ in both Eqs. (15.42) and (15.56). As in the case of the $C-H$-bond MO, $C_1 = 0.75$ based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is also one, and the energy matching condition is determined by the C_2 parameter. Using the energy of S, $E(S) = -10.36001\ eV$ in Eq. (15.65), the hybridization factor C_2 of Eq. (15.52) for the $S-H$-bond MO is

$$C_2(S3p\ to\ H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001\ eV}{-13.60580\ eV} = 0.76144 \tag{15.126}$$

Since the energy of S is matched to the Coulombic energy between the electron and proton of H, $E(H(a_0))$, $E_{initial}(c_{4\ AO/HO}) = E(H(a_0)) = -13.60580\ eV$, $E_{initial}(c_{5\ AO/HO}) = E(H) = -13.59844\ eV$, and E_{mag} is that corresponding to $E(H(a_0))$ given by Eq. (15.58). $E_D(Group)$ for hydrogen sulfide is equivalent to that of the SH functional group, and the $E_D(Group)$ (eV) for dihydrogen sulfide follows the same derivation as that for the SH functional group except that the parameters correspond to $n_1 = 2$ rather than $n_1 = 1$ in Eqs. (15.42) and (15.56).

Furthermore, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the $C-S$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with $E(AO/HO) = 0$ and $E_{\gamma'}(AO/HO) = \Delta E_{H_2MO}(AO/HO)$. Then, the solution of the $C-S$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243), c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489\ eV$ (Eq. (15.25)), and the S AO has an energy of $E(S) = -10.36001\ eV$. To meet the equipotential condition of the union of the

$C-S$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.51) for the $C-S$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ \mathrm{S}\right)=\frac{E(S)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right)=\frac{-10.36001\ eV}{-14.63489\ eV}(0.91771)=0.64965 \quad (15.127)$$

Since the sulfur is energy matched to $E\left(H\left(a_0\right)\right)$ in the $S-H$-bond MO, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-S$-bond MO in Eq. (15.52) due to the charge donation from the C and S atoms to the MO is $-0.72457\ eV$ corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The $C-C$ bonds to the $HCSH$ group (one H bond to C) were each treated as an iso $C-C$ bond. The $C-C$ bonds to the CSH group (no H bonds to C) were each treated as a tert-butyl $C-C$. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.79-15.108) are given in Table 15.152.

Table 15.147. The symbols of functional groups of alkyl thiols.

Functional Group	Group Symbol
SH group	SH
H_2S	H_2S
C-S	$C-S$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.148. The geometrical bond parameters of alkyl thiols and experimental values [1].

Parameter	$S-H\ (H_2S)$	SH Group	$C-S$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.83762	1.83762	1.90975	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.26842	1.26842	1.71455	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (A)$	1.34244	1.34244	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.3356	1.34066 (hydrogen sulfide) 1.34 (methanethiol)	1.819 (methanethiol) 1.829 (ethanethiol)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.32964	1.32964	0.84112	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.69025	0.69025	0.89778	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.149. The MO to HO intercept geometrical bond parameters of alkyl thiols. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{initial}$ $\left(a_0\right)$	r_{final} $\left(a_0\right)$	$E_{Coulomb}$ (eV) Final	$E\left(C'2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 $\left(a_0\right)$	d_2 $\left(a_0\right)$
$S-H$ (hydrogen sulfide) (dihydrogen sulfide)	S	0.55100	0	0	0		1.32010	1.23465	-11.01999		108.65	71.35	61.62	0.87355	0.39487
$RS-H$	S	-0.36229	0.55100	0	0		1.32010	0.92955	-14.63704		87.09	92.91	44.28	1.31557	0.04714
C'_aH_3-SH	S	-0.36229	0.55100	0	0		1.32010	0.92955	-14.63704		132.06	47.94	55.13	1.09181	0.62274
C'_aH_3-SH	C'_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	69.84	110.16	88.87	0.03762	1.67692
$RC'_bH_2C'_aH_2-C'_aH_3SH$	C'_a	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
$C'-H\left(C'H_3\right)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\left(CH_2\right)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\left(C'H\right)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2C'H_2-$ $(C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2C'H_2-$ $(C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b\left(H_2C_c-R'\right)HC'H_2-$ $(C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a\left(R'-H_2C_d\right)C'_b\left(R''-H_2C_e\right)C'H_2-$ $(C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b\left(H_2C_c-R'\right)HCH_2-$ $(C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C_e\right)CH_2-$ $(C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b\left(H_2C_c-R'\right)HCH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C_e\right)CH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.150. The energy parameters (eV) of functional groups of alkyl thiols.

Parameters	H_2S	SH Group	$C-S$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.75	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.76144	0.76144	0.64965	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	1	0	0	1	1	0	0	0	1	1	0
c_4	1	1	2	1	1	1	2	2	2	2	2	2
c_5	1	1	0	3	2	1	0	0	0	0	0	0
$C_{1\sigma}$	0.75	0.75	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{2\sigma}$	0.76144	0.76144	0.64965	1	1	1	1	1	1	1	1	1
V_c (eV)	-72.80662	-36.40331	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	21.45310	10.72655	7.93551	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	19.81003	9.90502	12.13899	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-9.90502	-4.95251	-6.06949	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\sigma\ \pi\sigma)$ (eV)	-20.72002	-10.36001	0	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{\pi_2\pi\sigma}(\sigma\ \pi\sigma)$ (eV)	1.10200	0.55100	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(\sigma\ \pi\sigma)$ (eV)	-19.61802	-10.91101	0.72457	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(\pi_2\pi\sigma)$ (eV)	-63.27052	-31.63526	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	1.10200	0.55100	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(\pi\sigma)$ (eV)	-62.16874	-31.08437	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	12.5415	12.5415	30.5436	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	8.25504	8.25504	20.10434	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{ii}$ (eV)	-0.17669	-0.17669	-0.28705	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kmb}$ (eV)	0.32422 [39]	0.33620 [40]	0.08146 [41]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{anc}$ (eV)	-0.01458	-0.00859	-0.24632	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{aug} (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(\pi\pi\sigma)$ (eV)	-31.10493[a]	-31.09296	-32.60626	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{antist}(\sigma_1\ \sigma\sigma\ \pi\sigma)$ (eV)	-13.60580	-13.60580	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{antist}(\sigma_2\ \sigma\sigma\ \pi\sigma)$ (eV)	-13.59844	-13.59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{\Pi}(\pi\pi\sigma)$ (eV)	3.78628	3.77430	3.33648	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

[a] $E_T(\pi\text{-}s,\pi_2 s) = E_T(\pi_2 s) - E_T(\pi s) = 62.19789\ eV - \left(-31.09296\ eV\right)$.

Table 15.151. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values base composition is given by (15.58).

Formula	Name	H_2S Group	SH Group	$C-S$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
HS	Hydrogen Sulfide	1	1	0	0	0	0	0	0	0	0	0	0	0	3.77430	3.653	-0.03320
H_2S	Dihydrogen Sulfide	0	1	0	0	0	0	0	0	0	0	0	0	0	7.56058	7.605	0.00582
CH_4S	Methanethiol	0	1	1	1	0	0	0	0	0	0	0	0	0	19.60264	19.575	-0.00141
C_2H_6S	Ethanethiol	0	1	1	1	1	0	1	0	0	0	0	0	0	31.76034	31.762	0.00005
C_3H_8S	1-Propanethiol	0	1	1	1	2	0	2	0	0	0	0	0	0	43.91804	43.933	0.00035
C_3H_8S	2-Propanethiol	0	1	1	2	0	1	0	2	0	0	0	0	0	44.01893	44.020	0.00003
$C_4H_{10}S$	1-Butanethiol	0	1	1	1	3	0	3	0	0	0	0	0	0	56.07574	56.089	0.00024
$C_4H_{10}S$	2-Butanethiol	0	1	1	2	1	1	1	2	0	0	0	0	0	56.17663	56.181	0.00009
$C_4H_{10}S$	2-Methyl-1-propanethiol	0	1	1	2	1	1	0	3	0	0	0	0	0	56.14830	56.186	0.00066
$C_4H_{10}S$	2-Methyl-2-propanethiol	0	1	1	3	0	0	0	0	3	0	0	0	-1	56.36027	56.313	-0.00084
$C_5H_{12}S$	2-Methyl-1-butanethiol	0	1	1	2	2	1	1	3	0	0	0	0	0	68.30600	68.314	0.00012
$C_5H_{12}S$	1-Pentanethiol	0	1	1	1	4	0	4	0	0	0	0	0	0	68.23344	68.264	0.00044
$C_5H_{12}S$	2-Methyl-2-butanethiol	0	1	1	3	1	0	1	0	3	0	0	0	-1	68.51797	68.441	-0.00113
$C_5H_{12}S$	3-Methyl-2-butanethiol	0	1	1	3	0	2	0	3	0	1	0	0	0	68.31552	68.381	0.00095
$C_5H_{12}S$	2,2-Dimethyl-1-propanethiol	0	1	1	3	1	0	1	0	3	0	0	0	-1	68.51797	68.461	-0.00084
$C_6H_{14}S$	1-Hexanethiol	0	1	1	1	5	0	5	0	0	0	0	0	0	80.39114	80.416	0.00031
$C_6H_{14}S$	2-Methyl-2-pentanethiol	0	1	1	3	2	0	2	0	3	0	0	0	-1	80.67567	80.607	-0.00085
$C_6H_{14}S$	2,3-Dimethyl-2-butanethiol	0	1	1	4	0	1	0	2	2	0	0	1	-1	80.71992	80.603	-0.00145
$C_7H_{16}S$	1-Heptanethiol	0	1	1	1	6	0	6	0	0	0	0	0	0	92.54884	92.570	0.00023
$C_{10}H_{22}S$	1-Decanethiol	0	1	1	1	9	0	9	0	0	0	0	0	0	129.02194	129.048	0.00020

Table 15.152. The bond angle parameters of alkyl thiols and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Conbumbo}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Conbumbo}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HSC_a$	2.53685	3.42910	4.5166	-10.36001 S	7	-15.75493 C_a	S	0.76144 (Eq. 15.125))	0.86359	0.75	1	0.75	1.13415	0				97.28	96.5 (methanethiol) 96.4 (ethanethiol)
$\angle C_bC_aS$	2.91547	3.42910	5.2344	-16.68412 C_b	25	-10.36001 S	S	0.81549	0.64965 (Eq. (15.127))	1	0.64965 (Eq. (15.127))	1	0.73257	-0.72457				110.92	108.3 (ethanethiol)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

SULFIDES ($C_nH_{2n+2}S_m$, $n=2,3,4,5...\infty$)

The alkyl sulfides, $C_nH_{2n+2}S_m$, comprise two types of $C-S$ functional groups, one for t-butyl groups corresponding to the C and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each $C-S$ group is solved by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243), c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. As in the case of thiols, C_2 of Eq. (15.52) for the $C-S$-bond MO given by Eq. (15.127) is $C_2\left(C2sp^3HO\ to\ \mathrm{S}\right)=0.64965$.

The $C-S$ group of alkyl sulfides is equivalent to that of thiols where $E_T\left(atom-atom,msp^3.AO\right)$ is $-0.72457\ eV$ (Eq. (14.151)). The t-butyl-$C-S$ group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table 15.153. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the $C-S$ bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus –c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the –x-axis for C. The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum

over the integer multiple of each $E_D(Group)$ of Table 15.156 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.79-15.108) are given in Table 15.158.

Table 15.153. The symbols of functional groups of alkyl sulfides.

Functional Group	Group Symbol
C-S (methyl, alkyl)	$C-S$ (i)
C-S ($(CH_3)_3C-S-$)	$C-S$ (ii)
CH_3 group	$C'-H\ (CH_3)$
CH_2 group	$C'-H\ (CH_2)$
CH	$C'-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C'-C'$ (b)
CC bond (tert-C)	$C'-C'$ (c)
CC (iso to iso-C)	$C'-C'$ (d)
CC (t to t-C)	$C'-C'$ (e)
CC (t to iso-C)	$C'-C'$ (f)

Table 15.154. The geometrical bond parameters of alkyl sulfides and experimental values [1].

Parameter	$C-S$ (i) Group	$C-S$ (ii) Group	$C'-H\ (CH_3)$ Group	$C'-H\ (CH_2)$ Group	$C'-H$ Group	$C-C$ (a) Group	$C'-C'$ (b) Group	$C'-C'$ (c) Group	$C'-C'$ (d) Group	$C'-C'$ (e) Group	$C'-C'$ (f) Group
$a\ (a_0)$	1.90975	1.90975	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.71455	1.71455	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\text{Å})$	1.81460	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.807 (dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	1.807 (dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.84112	0.84112	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.89778	0.89778	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.155. The MO to HO intercept geometrical bond parameters of alkyl sulfides. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, nsp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ $\left(a_0\right)$	r_{final} $\left(a_0\right)$	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 $\left(a_0\right)$	d_2 $\left(a_0\right)$
$R-S-R$ ($C-S$ (i) and (ii))	S	-0.36229	-0.36229	0	0		1.32010	0.87495	-15.55033		129.96	50.04	52.88	1.15262	0.56193
$H_3C_a-S-C_bH_2CH_2R$ ($C-S$ (i))	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.79	49.21	53.75	1.12937	0.58518
$H_3C_a-S-C_bH_2CH_2R$ ($C-S$ (i))	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
$H_3C_a-S-C_c(CH_3)_3$ ($C-S$ (i) and (ii))	C_c	-0.36229	-0.72457	-0.72457	-0.72457	-154.15170	0.91771	0.78367	-17.36176	-17.17090	125.97	54.03	48.94	1.25430	0.46025
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.156. The energy parameters (eV) of functional groups of alkyl sulfides.

Parameters	$C-S$ (i) Group	$C-S$ (ii) Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.64965	0.64965	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
$C_{1\omega}$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{2\omega}$	0.64965	0.64965	1	1	1	1	1	1	1	1	1
V_e (eV)	-46.36495	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	7.93551	7.93551	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12.13899	12.13899	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ni} (eV)	-6.06949	-6.06949	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\omega\ no)$ (eV)	0	0	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{n_2 MO}(\omega\ no)$ (eV)	-0.72457	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(\omega\ no)$ (eV)	0.72457	0.72457	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2 MO)$ (eV)	-31.63537	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, nsp^3.AO\right)$ (eV)	-0.72457	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(no)$ (eV)	-32.35994	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	30.5436	8.92777	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	20.10434	5.87641	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_n$ (eV)	-0.28705	-0.15519	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Knb}$ (eV)	0.08146 [41]	0.08146 [41]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{nuc}$ (eV)	-0.24632	-0.11446	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{img} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-32.60626	-32.47440	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{initial}(e_1\ no\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(e_2\ no\ no)$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.33648	3.20462	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the E_{group} (eV) values based on composition is given by (15.58).

Formula	Name	$C-S$ (i) Group	$C-S$ (ii) Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6S	Dimethyl sulfide	2	0	2	0	0	0	0	0	0	0	0	0	31.65668	31.672	0.00048
C_3H_8S	Ethyl methyl sulfide	1	0	2	1	0	1	0	0	0	0	0	0	43.81438	43.848	0.00078
$C_4H_{10}S$	Diethyl sulfide	2	0	2	2	0	1	0	0	0	0	0	0	55.97208	56.043	0.00126
$C_4H_{10}S$	Methyl propyl sulfide	2	0	2	2	0	2	0	0	0	0	0	0	55.97208	56.029	0.00102
$C_4H_{10}S$	Isopropyl methyl sulfide	2	0	3	0	1	0	2	0	0	0	0	0	56.07297	56.115	0.00075
$C_5H_{12}S$	Butyl methyl sulfide	2	0	2	3	0	3	0	0	0	0	0	0	68.12978	68.185	0.00081
$C_5H_{12}S$	t-Butyl methyl sulfide	1	1	4	0	0	0	0	3	0	0	0	-1	68.28245	68.381	0.00144
$C_5H_{12}S$	Ethyl propyl sulfide	1	0	2	3	0	3	0	0	0	0	0	0	68.12978	68.210	0.00117
$C_5H_{12}S$	Ethyl isopropyl sulfide	2	0	3	2	1	1	2	0	0	0	0	0	68.23067	68.350	0.00174
$C_6H_{14}S$	Diisopropyl sulfide	2	0	4	0	2	0	4	0	0	0	0	0	80.48926	80.542	0.00065
$C_6H_{14}S$	Butyl ethyl sulfide	2	0	2	4	0	4	0	0	0	0	0	0	80.28748	80.395	0.00133
$C_6H_{14}S$	Methyl pentyl sulfide	2	0	2	4	0	4	0	0	0	0	0	0	80.28748	80.332	0.00056
$C_8H_{18}S$	Dibutyl sulfide	2	0	2	6	0	6	0	0	0	0	0	0	104.60288	104.701	0.00094
$C_8H_{18}S$	Di-sec-butyl sulfide	2	0	4	2	2	2	4	0	0	0	0	0	104.80466	104.701	-0.00099
$C_8H_{18}S$	Di-t-butyl sulfide	0	2	6	0	0	0	0	6	0	0	0	-2	104.90822	104.920	0.00011
$C_8H_{18}S$	Diisobutyl sulfide	2	0	4	2	2	0	6	0	0	0	0	0	104.74800	104.834	0.00082
$C_{10}H_{22}S$	Dipentyl sulfide	2	0	2	8	0	8	0	0	0	0	0	0	128.91828	128.979	0.00047
$C_{10}H_{22}S$	Diisopentyl sulfide	2	0	4	4	2	2	6	0	0	0	0	0	129.06340	129.151	0.00068

Table 15.158. The bond angle parameters of alkyl sulfides and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\{atom-atom,msp^3.AO\}$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E'_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c'_2	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_aSC_a$ ($C-S$ (i))	3.42910	3.42910	5.2173	-16.11722	11	-16.11722	11	0.84418	0.84418	1	1	1	0.84418	-1.85836				99.06	99.05 (dimethyl sulfide)
$\angle C_aSC_b$ ($C-S$ (i))	3.42910	3.42910	5.1381	-15.75493 methyl C_a	7	-16.68412 methylene C_b	25	0.86359	0.81549	1	1	1	0.83954	-1.85836				97.04	97 (ethyl methyl sulfide)
$\angle SC_aC_b$ ($C-S$ (ii))	3.42910	2.91547	5.3364	-10.36001	S	-16.27490	15	0.64965 (Eq. (15.127))	0.83600	1	0.64965 (Eq. (15.127))	1	0.74282	-0.72457				114.27	114.0 (ethyl methyl sulfide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	109.3 (dimethyl sulfide) 110 (ethyl methyl sulfide)
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

DISULFIDES ($C_nH_{2n+2}S_{2m}$, $n=2,3,4,5...\infty$)

The alkyl disulfides, $C_nH_{2n+2}S_{2m}$, comprise $C-S$ and $S-S$ functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each $C-S$ group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulifides, C_2 of Eq. (15.52) for the $C-S$-bond MO given by Eq. (15.127) is $C_2\left(C2sp^3HO\ to\ \mathrm{S}\right)=0.64965$ and $E_T\left(atom-atom,msp^3.AO\right)$ is $-0.72457\ eV$ (Eq. (14.151)).

The $S-S$ group is solved as an H_2-type-ellipsoidal-MO that is energy matched to the energy of sulfur, $E\left(S\right)=-10.36001\ eV$, such that $E\left(AO/HO\right)=-10.36001\ eV$ in Eq. (15.42) with $E_T\left(AO/HO\right)=E\left(AO/HO\right)$. The $S-S$-bond MO is further energy matched to the $C2sp^3$ HO of the $C-S$-bond MO. C_2 of Eq. (15.52) for the $S-S$-bond MO given by Eq. (15.127) is also $C_2\left(C2sp^3HO\ to\ \mathrm{S}\right)=0.64965$. In order to match $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-S$ group ($-0.72457\ eV$ (Eq. (14.151))), $E_T\left(atom-atom,msp^3.AO\right)$ of the $S-S$-bond MO is determined using a linear combination of the AOs corresponding to $-0.72457\ eV$ and $0\ eV$ in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is $E_T\left(atom-atom,msp^3.AO\right)=-0.36229\ eV$.

The symbols of the functional groups of branched-chain alkyl disulfides are given in Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given

in Table 15.163 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.162 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.79-15.108) are given in Table 15.164.

Table 15.159. The symbols of functional groups of alkyl disulfides.

Functional Group	Group Symbol
C-S	$C-S$
S-S	$S-S$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.160. The geometrical bond parameters of alkyl disulfides and experimental values [1].

Parameter	$C-S$ (i) Group	$S-S$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.90975	2.37173	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.71455	1.91070	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.81460	2.02220	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.816 (dimethyl disulfide)	2.029 (dimethyl disulfide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.84112	1.40510	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.89778	0.80562	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.161. The MO to HO intercept geometrical bond parameters of alkyl disulfides. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, ntsp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RS-SR$ ($C-S$ (i) and (ii))	S	-0.36229	-0.18114	0	0		1.32010	0.88527	-15.36918		94.25	85.75	38.93	1.84513	0.06558
$H_3C_a-SS-C_bH_2CH_2R$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.79	49.21	53.75	1.12937	0.58518
$H_3C_a-SS-C_bH_2CH_2R$ ($C-S$ (i))	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
	C_c	-0.36229	-0.72457	-0.72457	-0.72457	-154.15170	0.91771	0.78367	-17.36176	-17.17090	125.97	54.03	48.94	1.25430	0.46025
$C-H\left(CH_3\right)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_2\right)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\left(CH\right)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0 72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.162. The energy parameters (eV) of functional groups of alkyl disulfides.

Parameters	$C-S$ (i) Group	$S-S$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.64965	0.64965	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1u}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2u}	0.64965	0.64965	1	1	1	1	1	1	1	1	1
V_c (eV)	-46.36495	-31.74215	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	7.93551	7.12083	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12.13899	6.69177	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{pi} (eV)	-6.06949	-3.34589	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\omega\ no)$ (eV)	0	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{\pi,SIG}(\omega\ no)$ (eV)	-0.72457	0	0	0	0	0	0	0	0	0	0
$E_T(\omega\ no)$ (eV)	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2,\omega)$ (eV)	-31.63537	-31.63544	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,nsp^3.AO\right)$ (eV)	-0.72457	-0.36229	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_\gamma(\omega)$ (eV)	-32.35994	-31.99766	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	30.5436	6.45076	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	20.10434	4.24600	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{\pi}$ (eV)	-0.28705	-0.13044	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kreb}$ (eV)	0.08146 [41]	0.06745 []	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{\omega\pi}$ (eV)	-0.24632	-0.09672	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-32.60626	-32.09437	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{unfold}(\omega\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{unfold}(\omega\ no)$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.33648	2.82459	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.163. The total bond energies of alkyl disulfides calculated using the functional group composition and the energies of Table 15.162 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by (15.58).

Formula	Name	$C-S$ Group	$S-S$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6S_2$	Dimethyl disulfide	2	1	2	0	0	0	0	0	0	0	0	0	34.48127	34.413	-0.00199
$C_4H_{10}S_2$	Diethyl disulfide	2	1	2	2	0	2	0	0	0	0	0	0	58.79667	58.873	0.00129
$C_6H_{14}S_2$	Dipropyl disulfide	2	1	2	0	4	4	0	0	0	0	0	0	83.11207	83.169	0.00068
$C_8H_{18}S_2$	Di-t-butyl disulfide	2	1	6	0	0	0	0	6	0	0	0	-2	107.99653	107.919	-0.00072

Table 15.164. The bond angle parameters of alkyl disulfides and experimental values [1]. In the calculation of θ_e, the parameters from the preceding angle were used. E_T is $E_T\{atom-atom, nsp^3.AO\}$.

Atoms of Angle	$2c'$ Bond 1 (a_p)	$2c'$ Bond 2 (a_p)	$2c'$ Terminal Atoms (a_p)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle SC_aH$															70.56			109.44	111.3 (dimethyl disulfide)
$\angle HC_aS$	2.09711	3.42910	4.6220	-15.55033 C_a	S	-10.36001 S	5	0.87495	0.76144 (Eq. (15.126))	0.75	0.76144 (Eq. 15.126))	0.75	0.87026	0				111.22	111.3 (dimethyl disulfide)
$\angle SSC_a$	3.82141	3.42910	5.7017	-10.36001 S	S	-14.82575 C_a	1	0.64965 (Eq. (15.127))	0.91771	1	0.64965 (Eq. (15.127))	1	0.78368	-0.72457				103.57	103.2 (dimethyl disulfide)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ ten C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

SULFOXIDES ($C_nH_{2n+2}(SO)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfoxides, $C_nH_{2n+2}(SO)_m$, comprise a $C-SO-C$ moiety that comprises $C-S$ and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\,eV$ (Eq. (15.25)), and the S AO has an initial energy of $E(S)=-10.36001\,eV$ [38]. To meet the equipotential condition of the union of the $S=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $S=O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O\ to\ S3sp^3\ to\ C2sp^3HO) &= \frac{E(O)}{E(S)}c_2(C2sp^3HO) \\ &= \frac{-13.61806\,eV}{-10.36001\,eV}(0.91771) \\ &= 1.20632 \end{aligned} \tag{15.128}$$

The S atom also forms a single bond with each of the $C2sp^3$ HOs of the two $C-S$ groups. The formation of these bonds is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement:

$3sp^3$ state

↑	↑	↑	↑
0,0	1,-1	1,0	1,1

(15.129)

where the quantum numbers (ℓ, m_ℓ) are below each electron. The $3s$ shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}\left(S,3sp^3\right)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.118) with $r_{3sp^3}=1.17585a_0$ (Eq. (15.119)) is $-11.57099\ eV$. Using Eq. (15.16) with the radius of the sulfur atom $r_{16}=1.32010a_0$ given by Eq. (10.341), the energy $E\left(S3sp^3\right)$ of the outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}\left(S3sp^3\right)$ and $E(magnetic)$:

$$\begin{aligned}E\left(S3sp^3\right)&=\frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_{16}^3}\\&=\frac{-e^2}{8\pi\varepsilon_0 1.17585a_0}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(1.32010a_0\right)^3}\\&=-11.57099\ eV+0.04973\\&=-11.52126\ eV\end{aligned}\tag{15.130}$$

Then, the hybridization energy $E_{hybridization}\left(S3sp^3\right)$ of the $S3sp^3$ HO is

$$\begin{aligned}E_{hybridization}\left(S3sp^3\right)&=E\left(S3sp^3\right)-E\left(S\right)\\&=-11.52126\ eV-10.36001\ eV\\&=-1.16125\ eV\end{aligned}\tag{15.131}$$

The SO group is matched to the $C-S$ group with which it shares the common hybridized S atom. Consequently, $E_{hybridization}\left(S3sp^3\right)$ is subtracted from $E_T\left(Group\right)$ in the determination of $E_D\left(Group\right)$ (Eq. 15.56)). Furthermore, the energy of the $S=O$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that $E\left(AO/HO\right)=E\left(S3sp^3\right)=-11.52126\ eV$ and $\Delta E_{H_2MO}\left(AO/HO\right)=E_{hybridization}\left(S3sp^3\right)=-1.16125\ eV$. Then, $E_T\left(AO/HO\right)=E\left(S\right)=-10.36001\ eV$. Also, $E_T\left(atom-atom,msp^3.AO\right)$ of the $S=O$ bond is zero since there are no bonds with a $C2sp^3$ HO.

The $C-S$ group is solved as an energy minimum by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell and by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the $S3sp^3$ shell, $E_{Coulomb}\left(S3sp^3\right)$ given by Eq. (15.120) in Eq. (15.63), the $S3sp^3$-shell hybridization factor, $c_2\left(S3sp^3\right)$, is

$$c_2\left(S3sp^3\right)=\frac{E_{Coulomb}\left(S3sp^3\right)}{E(H)}=\frac{-11.57099\ eV}{-13.60580\ eV}=0.85045 \tag{15.132}$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E\left(S3sp^3\right)=-11.52126\ eV$ (Eq. (15.130)). To meet the equipotential condition of the union of the $C-S$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-S$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right)=\frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right)=\frac{-11.52126\ eV}{-14.63489\ eV}(0.85045)=0.66951 \tag{15.133}$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the $C-S$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with $E_{(AO/HO)}=0$ and $E_T\left(AO/HO\right)=\Delta E_{H_2MO}\left(AO/HO\right)$. For sulfoxides, $\Delta E_{H_2MO}\left(AO/HO\right)=-0.72457\ eV$. Further equivalently, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the $C-S$ bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus –c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the –x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	$C-S$
SO	SO
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

Parameter	$C-S$ Group	SO Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.87325	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.67271	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\text{Å})$	1.77031	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.799 (dimethyl sulfoxide)	1.485 (dimethyl sulfoxide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.84328	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.89294	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides. R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\ (a_0)$	$d_2\ (a_0)$
$R_2S=O$	S	0	-0.36229	-0.36229	0		1.32010	0.87495	-15.55033		79.78	100.22	38.00	1.56425	0.15529
$R_2S=O$	O	0	0	0	0		1.00000	0.91771	-14.82575		84.06	95.94	40.75	1.50400	0.09304
R_2-SO	S	-0.36229	-0.36229	0	0		1.32010	0.87495	-15.55033		129.35	50.65	53.36	1.11799	0.55472
$H_3C_a-S(O)-C_bH_2CH_2R$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.19	49.81	54.24	1.09461	0.57809
$H_2C_a-S(O)-C_bH_2CH_2R$	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.05	51.95	52.03	1.15245	0.52026
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_2C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ ($C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b(H_2C_c-R')HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a(R'-H_2C_d)C_b(R''-H_2C_e)CH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfoxides.

Parameters	$C-S$ Group	SO Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.66951	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	4	1	1	1	2	2	2	2	2	2
c_5	0	1	3	2	1	0	0	0	0	0	0
$C_{1\sigma}$	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
$C_{2\sigma}$	0.66951	1	1	1	1	1	1	1	1	1	1
$V_c\ (eV)$	-46.73032	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
$V_p\ (eV)$	8.13401	19.31325	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
$T\ (eV)$	12.47306	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
$V_m\ (eV)$	-6.23653	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\sigma\sigma\ mo)\ (eV)$	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2SO}(\sigma\sigma\ mo)\ (eV)$	-0.72457	-1.16125	0	0	0	0	0	0	0	0	0
$E_T(\sigma\sigma\ mo)\ (eV)$	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2SO)\ (eV)$	-31.63521	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(SO)\ (eV)$	-32.35994	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\ \left(10^{15}\ rad/s\right)$	30.8880	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_K\ (eV)$	20.33104	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D\ (eV)$	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kvib}\ (eV)$	0.08543 [42]	0.12832 [43]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{esc}\ (eV)$	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{nuc}\ (eV)$	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-32.60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(\sigma_1.\sigma\sigma\ mo)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(\sigma_2.\sigma\sigma\ mo)\ (eV)$	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)\ (eV)$	3.33611	3.86856	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula	Name	$C-S$ Group	SO Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6SO	Dimethyl sulfoxide	2	1	2	0	0	0	0	0	0	0	0	35.52450	35.435	-0.00253
$C_4H_{10}SO$	Diethyl sulfoxide	2	1	2	2	0	2	0	0	0	0	0	59.83990	59.891	0.00085
$C_6H_{14}SO$	Dipropyl sulfoxide	2	1	2	4	0	4	0	0	0	0	0	84.15530	84.294	0.00165

Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of θ_e, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_\beta S C_\alpha$	3.34541	3.34541	4.9800	-16.47951	21	-16.47951	21	0.82562	0.82562	1	1	1	0.82562	-1.85836				96.20	96.6 (dimethyl sulfoxide)
$\angle C_\alpha S O$	3.34541	2.81792	4.9598	-15.18804 C_α	2	-13.61806 O	O	0.89582	0.85395 (Eq. (15.114))	1	1	1	0.87489	-1.65376				106.88	106.7 (dimethyl sulfoxide)
Methylene $\angle HC_\alpha H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_\alpha C_b C_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_\alpha C_b H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_\alpha H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	110.3 (dimethyl sulfoxide)
$\angle C_\alpha C_b C_c$															70.56			109.44	
$\angle C_\alpha C_b H$															70.56			109.44	
$\angle C_b C_\alpha C_c$ iso C_α	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_b C_\alpha H$ iso C_α	2.91547	2.11323	4.1633	-15.55033 C_α	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_b C_\alpha H$ iso C_α	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_α	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_b C_\alpha C_c$ tert C_α	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_b C_\alpha C_d$															72.50			107.50	

SULFOXIDES ($C_nH_{2n+2}(SO)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfoxides, $C_nH_{2n+2}(SO)_m$, comprise a $C-SO-C$ moiety that comprises $C-S$ and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\ eV$ (Eq. (15.25)), and the S AO has an initial energy of $E(S)=-10.36001\ eV$ [38]. To meet the equipotential condition of the union of the $S=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $S=O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O\ to\ S3sp^3\ to\ C2sp^3HO) &= \frac{E(O)}{E(S)}c_2(C2sp^3HO) \\ &= \frac{-13.61806\ eV}{-10.36001\ eV}(0.91771) \\ &= 1.20632 \end{aligned} \tag{15.128}$$

The S atom also forms a single bond with each of the $C2sp^3$ HOs of the two $C-S$ groups. The formation of these bonds is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement:

$3sp^3$ state

↑	↑	↑	↑
0,0	1,-1	1,0	1,1

(15.129)

where the quantum numbers (ℓ, m_ℓ) are below each electron. The $3s$ shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}\left(S,3sp^3\right)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.118) with $r_{3sp^3}=1.17585a_0$ (Eq. (15.119)) is $-11.57099\ eV$. Using Eq. (15.16) with the radius of the sulfur atom $r_{16}=1.32010a_0$ given by Eq. (10.341), the energy $E\left(S3sp^3\right)$ of the outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}\left(S3sp^3\right)$ and $E(magnetic)$:

$$\begin{aligned}E\left(S3sp^3\right)&=\frac{-e^2}{8\pi\varepsilon_0 r_{3sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_{16}^3}\\&=\frac{-e^2}{8\pi\varepsilon_0 1.17585a_0}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(1.32010a_0\right)^3}\\&=-11.57099\ eV+0.04973\\&=-11.52126\ eV\end{aligned}\tag{15.130}$$

Then, the hybridization energy $E_{hybridization}\left(S3sp^3\right)$ of the $S3sp^3$ HO is

$$\begin{aligned}E_{hybridization}\left(S3sp^3\right)&=E\left(S3sp^3\right)-E\left(S\right)\\&=-11.52126\ eV-10.36001\ eV\\&=-1.16125\ eV\end{aligned}\tag{15.131}$$

The SO group is matched to the $C-S$ group with which it shares the common hybridized S atom. Consequently, $E_{hybridization}\left(S3sp^3\right)$ is subtracted from $E_T\left(Group\right)$ in the determination of $E_D\left(Group\right)$ (Eq. 15.56)). Furthermore, the energy of the $S=O$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that $E\left(AO/HO\right)=E\left(S3sp^3\right)=-11.52126\ eV$ and $\Delta E_{H_2MO}\left(AO/HO\right)=E_{hybridization}\left(S3sp^3\right)=-1.16125\ eV$. Then, $E_T\left(AO/HO\right)=E\left(S\right)=-10.36001\ eV$. Also, $E_T\left(atom-atom,msp^3.AO\right)$ of the $S=O$ bond is zero since there are no bonds with a $C2sp^3$ HO.

The $C-S$ group is solved as an energy minimum by hybridizing the $2s$ and $2p$ AOs of the C atom to form a single $2sp^3$ shell and by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the $S3sp^3$ shell, $E_{Coulomb}\left(S3sp^3\right)$ given by Eq. (15.120) in Eq. (15.63), the $S3sp^3$-shell hybridization factor, $c_2\left(S3sp^3\right)$, is

$$c_2\left(S3sp^3\right)=\frac{E_{Coulomb}\left(S3sp^3\right)}{E(H)}=\frac{-11.57099\ eV}{-13.60580\ eV}=0.85045 \tag{15.132}$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E\left(S3sp^3\right)=-11.52126\ eV$ (Eq. (15.130)). To meet the equipotential condition of the union of the $C-S$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the $C-S$-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right)=\frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right)=\frac{-11.52126\ eV}{-14.63489\ eV}(0.85045)=0.66951 \tag{15.133}$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the $C-S$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with $E_{(AO/HO)}=0$ and $E_T\left(AO/HO\right)=\Delta E_{H_2MO}\left(AO/HO\right)$. For sulfoxides, $\Delta E_{H_2MO}\left(AO/HO\right)=-0.72457\ eV$. Further equivalently, $E_T\left(atom-atom,msp^3.AO\right)=-0.72457\ eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the $C-S$ bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus –c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the –x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	$C-S$
SO	SO
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

Parameter	$C-S$ Group	SO Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.87325	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.67271	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (A)$	1.77031	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.799 (dimethyl sulfoxide)	1.485 (dimethyl sulfoxide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.84328	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.89294	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Coulomb}$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\ (a_0)$	$d_2\ (a_0)$
$R_2S=O$	S	0	-0.36229	-0.36229	0		1.32010	0.87495	-15.55033		79.78	100.22	38.00	1.56425	0.15529
$R_2S=O$	O	0	0	0	0		1.00000	0.91771	-14.82575		84.06	95.94	40.75	1.50400	0.09504
R_2-SO	S	-0.36229	-0.36229	0	0		1.32010	0.87495	-15.55033		129.35	50.65	53.36	1.11799	0.55472
$H_3C_a-S(O)-C_bH_2CH_2R$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	130.19	49.81	54.24	1.09461	0.57809
$H_3C_a-S(O)-C_bH_2CH_2R$	C_b	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	128.05	51.95	52.03	1.15245	0.52026
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ ($C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C'-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C'-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C-C'$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ ($C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ ($C'-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfoxides.

Parameters	$C-S$ Group	SO Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	0.66951	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	2	4	1	1	1	2	2	2	2	2	2
c_5	0	1	3	2	1	0	0	0	0	0	0
C_{1n}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2n}	0.66951	1	1	1	1	1	1	1	1	1	1
V_s (eV)	-46.73032	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	8.13401	19.31325	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12.47306	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{sl} (eV)	-6.23653	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\text{no mo})$ (eV)	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2MO}(\text{no mo})$ (eV)	-0.72457	-1.16125	0	0	0	0	0	0	0	0	0
$E_T(\text{no mo})$ (eV)	0.72457	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2 MO)$ (eV)	-31.63521	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(MO)$ (eV)	-32.35994	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	30.8880	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	20.33104	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D$ (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kroh}$ (eV)	0.08543 [42]	0.12832 [43]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{rec}$ (eV)	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{atom} (eV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-32.60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{isolated}(e_1, no\ mo)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{isolated}(e_2, no\ mo)$ (eV)	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.33611	3.86856	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula	Name	$C-S$ Group	SO Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_2H_6SO	Dimethyl sulfoxide	2	1	2	0	0	0	0	0	0	0	0	35.52450	35.435	-0.00253
$C_4H_{10}SO$	Diethyl sulfoxide	2	1	2	2	0	2	0	0	0	0	0	59.83990	59.891	0.00085
$C_6H_{14}SO$	Dipropyl sulfoxide	2	1	2	4	0	4	0	0	0	0	0	84.15530	84.294	0.00165

Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of θ_e, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_T (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_a S C_a$	3.34541	3.34541	4.9800	-16.47951	21	-16.47951	21	0.82562	0.82562	1	1	1	0.82562	-1.85836				96.20	96.6 (dimethyl sulfoxide)
$\angle C_a S O$	3.34541	2.81792	4.9598	-15.18804 C_a	2	-13.61806 O	0	0.89582	0.85395 (Eq. (15.114))	1	1	1	0.87489	-1.65376				106.88	106.7 (dimethyl sulfoxide)
Methylene $\angle HC_a H$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_a C_b C_c$															69.51			110.49	112 (propane) 113.8 (butane) *110.8* (isobutane)
$\angle C_a C_b H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_a H$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	110.3 (dimethyl sulfoxide)
$\angle C_a C_b C_c$															70.56			109.44	
$\angle C_a C_b H$															70.56			109.44	
$\angle C_b C_a C_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_b C_a H$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_a C_b H$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_b C_a C_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_b C_a C_d$															72.50			107.50	

DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle $\theta_{\angle S=O/CSC}$ between the plane defined by the CSC MO comprising a linear combination of two $S-C$-bond MOs and a line defined by the $S=O$-bond MO where S is the central atom is calculated using the results given in Table 15.170 and Eqs. (15.105-15.108). The distance d_1 along the bisector of $\theta_{\angle CSC}$ from S to the internuclear-distance line between C and C, $2c'_{C-C}$, is given by

$$d_1 = 2c'_{S-C}\cos\frac{\theta_{\angle CSC}}{2} = 4.9800a_0\cos\frac{96.20°}{2} = 2.23423a_0 \tag{15.134}$$

where $2c'_{S-C}$ is the internuclear distance between S and C. The atoms C, C, and O define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle COC}$ can be solved from the internuclear distances between C and C, $2c'_{C-C}$, and between C and O, $2c'_{C-O}$, using the law of cosines (Eq. (15.106)):

$$\begin{aligned}\theta_{\angle COC} &= \cos^{-1}\left(\frac{\left(2c'_{C-O}\right)^2+\left(2c'_{C-O}\right)^2-\left(2c'_{C-C}\right)^2}{2\left(2c'_{C-O}\right)\left(2c'_{C-O}\right)}\right)\\ &= \cos^{-1}\left(\frac{\left(4.95984\right)^2+\left(4.95984\right)^2-\left(4.9800\right)^2}{2\left(4.95984\right)\left(4.95984\right)}\right)\\ &= 60.27°\end{aligned} \tag{15.135}$$

Then, the distance d_2 along the bisector of $\theta_{\angle COC}$ from O to the internuclear-distance line $2c'_{C-C}$, is given by

$$d_2 = 2c'_{C-O}\cos\frac{\theta_{\angle COC}}{2} = 4.95984a_0\cos\frac{60.27°}{2} = 4.28952a_0 \tag{15.136}$$

The lengths d_1, d_2, and $2c'_{S=O}$ define a triangle wherein the angle between d_1 and the internuclear distance between O and S, $2c'_{S=O}$, is the dihedral angle $\theta_{\angle S=O/CSC}$ that can be solved using the law of cosines (Eq. (15.108)):

$$\begin{aligned}\theta_{\angle S=O/CSC} &= \cos^{-1}\left(\frac{d_1^2+\left(2c'_{S=O}\right)^2-d_2^2}{2d_1\left(2c'_{S=O}\right)}\right)\\ &= \cos^{-1}\left(\frac{\left(2.23423\right)^2+\left(2.81792\right)^2-\left(4.28952\right)^2}{2\left(2.23423\right)\left(2.81792\right)}\right)\\ &= 115.74°\end{aligned} \tag{15.137}$$

The experimental [1] dihedral angle $\theta_{\angle S=O/C:SC}$ is

$$\theta_{\angle S=O/CSC} = 115.5° \qquad (15.138)$$

SULFITES ($C_nH_{2n+2}(SO_3)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfites, $C_nH_{2n+2}(SO_3)_m$, comprise a $C-O-SO-O-C$ moiety that comprises two types $C-O$ functional groups, one for methyl and one for alkyl, and $O-S$ and SO functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The SO functional group is equivalent to that of sulfoxides with $E_T(atom-atom,msp^3.AO)=0$ as given in the Sulfoxides section. The methyl and alkyl $C-O$ functional groups having $E_T(atom-atom,msp^3.AO)=-1.44915\,eV$ and $E_T(atom-atom,msp^3.AO)=-1.65376\,eV$, respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The SO functional group comprises a double bond between the S atom and the two unpaired electrons of O. The S atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the $O-S$ groups is between the sulfur atom and a $O2p$ AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the $S3p$ shell to give the orbital arrangement given by Eq. (15.129). Then, the Coulombic energy $E_{Coulomb}(S,3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.120) with $r_{3sp^3}=1.17585a_0$ (Eq. (15.119)) is $-11.57099\,eV$. Using Eq. (15.16) with the radius of the

sulfur atom $r_{16}=1.32010a_0$ given by Eq. (10.341), the energy $E\left(S3sp^3\right)$ of the outer electron of the $S3sp^3$ shell given by the sum of $E_{Coulomb}\left(S3sp^3\right)$ and $E(magnetic)$ is $E\left(S3sp^3\right)=-11.52126\ eV$ (Eq. (15.130)).

Thus, the $O-S$ group is solved as an energy minimum by hybridizing the four $S3p$ electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $O2p$ AO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. Each $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)), and the S HO has an energy of $E\left(S3sp^3\right)=-11.52126\ eV$. To meet the equipotential condition of the union of the $O-S$ H_2-type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a $C2sp^3$ HO, the hybridization factor C_2 of Eq. (15.52) for the $O-S$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} C_2\left(S3sp^3\ to\ O\ to\ C2sp^3HO\right) &= \frac{E\left(S,3sp^3\right)}{E(O,2p)}c_2\left(C2sp^3HO\right) \\ &= \frac{-11.52126\ eV}{-13.61806\ eV}(0.91771) \\ &= 0.77641 \end{aligned} \tag{15.139}$$

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the $O-S$-bond MO is the sum of the component energies of the H_2-type ellipsoidal MO given in Eq. (15.42) with $E\left(AO/HO\right)=0$ and $E_T\left(AO/HO\right)=\Delta E_{H_2MO}\left(AO/HO\right)$. For sulfites, $\Delta E_{H_2MO}\left(AO/HO\right)=-0.92918\ eV$ and equivalently, $E_T\left(atom-atom,msp^3.AO\right)=-0.92918\ eV$ (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.

The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 15.175 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.79-15.108) are given in Table 15.182.

Table 15.177. The symbols of functional groups of alkyl sulfites.

Functional Group	Group Symbol
C-O (methyl)	$C-O$ (i)
C-O (alkyl)	$C-O$ (ii)
O-SO_2	$O-S$
SO	SO
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.178. The geometrical bond parameters of alkyl sulfites and experimental values [1].

Parameter	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$	SO	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.80717	1.79473	1.70299	1.98517	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.34431	1.33968	1.48102	1.40896	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.42276	1.41785	1.56744	1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$			1.574 (H_2SO_4)	1.485 (dimethyl sulfoxide)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.20776	1.19429	0.84069	1.39847	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.74388	0.74645	0.86966	0.70974	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.179. The MO to HO intercept geometrical bond parameters of alkyl sulfites. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, nsp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$(RO)_2S=O_a$	S	0	-0.46459	-0.46459	0		1.52010	0.86359	-15.75493		78.56	101.44	37.25	1.58026	0.17130
$(RO)_2S=O_a$	O_a	0	0	0	0		1.00000	0.91771	-14.82575		84.06	95.94	40.75	1.50400	0.09504
$CH_3O_a-S(O)OR'$	S	-0.46459	-0.46459	0	0		1.52010	0.86359	-15.75493		126.68	53.32	55.47	0.96521	0.51581
$CH_3O_a-S(O)OR'$ $(C-O$ (i))	O_a	-0.46459	-0.72457	0	0		1.00000	0.84957	-16.01492		126.03	53.97	54.81	0.98133	0.49969
$RCH_2O_a-S(O)OR'$ $(C-O$ (ii))	O_a	-0.46459	-0.82688	0	0		1.00000	0.84418	-16.11722		125.77	54.23	54.56	0.98753	0.49349
$H_3C_a-O_aS(O)OR$ $(C-O$ (i))	O_a	-0.72457	-0.46459	0	0		1.00000	0.84957	-16.01492		93.85	86.15	44.57	1.28731	0.05700
$H_3C_a-O_aS(O)OR$ $(C-O$ (i))	C_a	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$RH_2C_a-O_aS(O)OR'$ $(C-O$ (ii))	O_a	-0.82688	-0.46459	0	0		1.00000	0.84418	-16.11722		94.50	85.50	44.80	1.27343	0.06624
$RH_2C_a-O_aS(O)OR'$ $(C-O$ (ii))	C_a	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.58181	-16.39095	92.41	87.59	43.35	1.30512	0.03456
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2C'H_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2C'H_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HC'H_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_aC_b\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)C'H_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50370
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_aC_b\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)C'H_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HC'H_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_aC_b\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)C'H_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.180. The energy parameters (eV) of functional groups of alkyl sulfites.

Parameters	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$ Group	SO Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	2	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85395	0.85395	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	0	0	1	1	0	0	0	1	1	0
c_4	2	2	2	4	1	1	1	2	2	2	2	2	2
c_5	0	0	0	1	3	2	1	0	0	0	0	0	0
C_{1v}	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2v}	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-33.15757	-33.47304	-48.93512	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	10.12103	10.15605	9.18680	19.31325	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	9.17389	9.32537	14.36741	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{nn} (eV)	-4.58695	-4.66268	-7.18371	-10.40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(xo\ no)$ (eV)	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2SO}(xo\ no)$ (eV)	-1.44915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0	0	0	0
$E_T(xo\ no)$ (eV)	-13.18574	-12.98113	0.92918	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_i xo)$ (eV)	-31.63533	-31.63544	-31.63543	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	-1.44915	-1.65376	-0.92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(xo)$ (eV)	-33.08452	-33.28912	-32.56455	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	22.0240	12.1583	33.4164	17.6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	14.49660	8.00277	21.99527	11.63476	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{ch}$ (eV)	-0.24921	-0.18631	-0.30214	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Keh}$ (eV)	0.13663 [21]	0.13663 [21]	0.08679 [42]	0.12832 [43]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{vac}$ (eV)	-0.18089	-0.11799	-0.25875	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{neg} (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-33.26541	-33.40711	-32.82330	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{indef}(c_i\ xo\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{indef}(c_i\ xo\ no)$ (eV)	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{Th}(Group)$ (eV)	3.99563	4.13733	3.55352	3.86856	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.181. The total bond energies of alkyl sulfites calculated using the functional group composition and the energies of Table 15.180 compared to the experimental values [3].

Formula	Name	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$ Group	SO Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_3$	Dimethyl sulfite	2	0	2	1	2	0	0	0	0	0	0	0	0	43.95058	44.042	0.00207
$C_4H_{10}SO_3$	Diethyl sulfite	0	2	2	1	2	2	0	2	0	0	0	0	0	68.54939	68.648	0.00143
$C_8H_{18}SO_3$	Dibutyl sulfite	0	2	2	1	2	6	0	6	0	0	0	0	0	117.18019	117.191	0.00009

Table 15.182. The bond angle parameters of alkyl sulfites and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,nsp^3.AO\right)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{C_{centrum}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{C_{endatomic}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle O_a S O_b$	2.81792	2.96203	4.6904	-15.95954 O_a	9	-16.11722 O_c	II	0.85252	0.84418	I	I	I	0.84835	-1.65376				108.46	
$\angle O_b S O_c$	2.96203	2.96203	4.6476	-16.11722 O_b	II	-16.11722 O_c	II	0.84418	0.84418	I	I	I	0.84418	-1.65376				103.35	
$\angle C_a O_b S$	2.68862	2.96203	4.8416	-15.75493 C_a	7	-10.36001 S	S	0.86359	0.77641 (Eq. (15.139))	I	0.77641 (Eq. (15.139))	I	0.82000	-0.72457				117.84	
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	I	I	I	0.75	1.15796	0				108.44	107 (propane)
$\angle C_a C_b C_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_a C_b H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	I	I	I	0.75	1.15796	0				109.50	
$\angle C_a C_b C_c$															70.56			109.44	
$\angle C_a C_b H$															70.56			109.44	
$\angle C_b C_a C_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	I	I	I	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_b C_a H$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	I	0.87495	0.91771	0.75	I	0.75	1.04887	0				110.76	
$\angle C_a C_b H$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	I	0.87495	0.91771	0.75	I	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_b C_a C_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	I	0.87495	0.91771	0.75	I	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_b C_a C_d$															72.50			107.50	

SULFATES ($C_nH_{2n+2}(SO_4)_m$, $n=2,3,4,5...\infty$)

The alkyl sulfates, $C_nH_{2n+2}(SO_4)_m$, comprise a $C-O-SO_2-O-C$ moiety that comprises two types $C-O$ functional groups, one for methyl and one for alkyl, and $O-S$ and SO_2 functional groups. The alkyl portion of the alkyl sulfate may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl $C-O$ functional groups having $E_T(atom-atom,msp^3.AO)=-1.44915\ eV$ and $E_T(atom-atom,msp^3.AO)=-1.65376\ eV$, respectively, are equivalent to the corresponding groups given in the Sulfites section. The $O-S$ functional group having $E_T(atom-atom,msp^3.AO)=-0.92918\ eV$ is equivalent to that given in the Sulfites section. The SO_2 functional group is equivalent to that of sulfones with $E_T(atom-atom,msp^3.AO)=0$ as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each $E_D(group)$ of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.79-15.108) are given in Table 15.188.

Table 15.183. The symbols of functional groups of alkyl sulfates.

Functional Group	Group Symbol
C-O (methyl)	$C-O$ (i)
C-O (alkyl)	$C-O$ (ii)
O-SO_3	$O-S$
SO_2	SO_2
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.184. The geometrical bond parameters of alkyl sulfates and experimental values [1].

Parameter	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$	SO_2	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.80717	1.79473	1.70299	1.85851	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.34431	1.33968	1.48102	1.36327	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.42276	1.41785	1.56744	1.44282	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$			1.574 (H_2SO_4)	1.435 (dimethyl sulfone)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	1.20776	1.19429	0.84069	1.26315	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.74388	0.74645	0.86966	0.73353	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl sulfates. R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$(RO)_2(O_a)S=O_a$	S	0	0	-0.46459	-0.46459		1.32010	0.86359	-15.75493		90.46	89.54	43.13	1.35635	0.00693
$(RO)_2(O_a)S=O_a$	O_a	0	0	0	0		1.00000	0.91771	-14.82575		95.05	84.95	46.36	1.28256	0.08071
$CH_3O_a-S(O_2)OR'$	S	-0.46459	-0.46459	0	0		1.32010	0.86359	-15.75493		126.68	53.32	55.47	0.96521	0.51581
$CH_3O_a-S(O_2)OR'$ $(C-O$ (i))	O_a	-0.46459	-0.72457	0	0		1.00000	0.84957	-16.01492		126.03	53.97	54.81	0.98133	0.49969
$RCH_2O_a-S(O_2)OR'$ $(C-O$ (ii))	O_a	-0.46459	-0.82688	0	0		1.00000	0.84418	-16.11722		125.77	54.23	54.56	0.98753	0.49349
$H_3C_a-O_aS(O_2)OR$ $(C-O$ (i))	O_a	-0.72457	-0.46459	0	0		1.00000	0.84957	-16.01492		93.85	86.15	44.57	1.28731	0.05700
$H_3C_a-O_aS(O_2)OR$ $(C-O$ (i))	C_a	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$RH_2C_a-O_aS(O_2)OR'$ $(C-O$ (ii))	O_a	-0.82688	-0.46459	0	0		1.00000	0.84418	-16.11722		94.50	85.50	44.80	1.27343	0.06624
$RH_2C_a-O_aS(O_2)OR'$ $(C-O$ (ii))	C_a	-0.82688	-0.92918	0	0	-153.37175	0.91771	0.82053	-16.58181	-16.39095	92.41	87.59	43.35	1.30512	0.03456
$C'-H\left(CH_3\right)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\left(CH_2\right)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\left(CH\right)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.186. The energy parameters (eV) of functional groups of alkyl sulfates.

Parameters	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$ Group	SO_2 Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	1	1	1	4	3	2	1	1	1	1	1	1	1
n_2	0	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85395	0.85395	1	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	0	1	1	0	0	0	1	1	0
c_4	2	2	2	8	1	1	1	2	2	2	2	2	2
c_5	0	0	0	1	3	2	1	0	0	0	0	0	0
C_{1v}	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2v}	1	1	0.77641	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-33.15757	-33.47304	-48.93512	-180.36454	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	10.12103	10.15605	9.18680	39.92103	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	9.17389	9.32537	14.36741	48.52397	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-4.58695	-4.66268	-7.18371	-24.26198	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(AO\ no)$ (eV)	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2NO}(AO\ no)$ (eV)	-1.44915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0	0	0	0
$E_T(AO\ no)$ (eV)	-13.18574	-12.98113	0.92918	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2NO)$ (eV)	-31.63533	-31.63544	-31.63543	-126.54154	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-1.44915	-1.65376	-0.92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(NO)$ (eV)	-33.08452	-33.28912	-32.56455	-126.54147	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	22.0240	12.1583	33.4164	11.5378	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	14.49660	8.00277	21.99527	7.59437	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\bar{E}_D$ (eV)	-0.24921	-0.18631	-0.30214	-0.17247	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\bar{E}_{Kvib}$ (eV)	0.13663 [21]	0.13663 [21]	0.08679 [42]	0.12832 [43]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\bar{E}_{rot}$ (eV)	-0.18089	-0.11799	-0.25875	-0.10831	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$\bar{E}_{trans}$ (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-33.26541	-33.40711	-32.82330	-126.97472	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{internal}(c_1.AO\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{internal}(c_2.AO\ no)$ (eV)	0	0	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	3.99563	4.13733	3.55352	8.61994	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.187. The total bond energies of alkyl sulfates calculated using the functional group composition and the energies of Table 15.186 compared to the experimental values [3].

Formula	Name	$C-O$ (i) Group	$C-O$ (ii) Group	$O-S$ Group	SO_2 Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_4$	Dimethyl sulfate	2	0	2	1	2	0	0	0	0	0	0	0	0	48.70617	48.734	0.00058
$C_4H_{10}SO_4$	Diethyl sulfate	0	2	2	1	2	2	0	2	0	0	0	0	0	73.30077	73.346	0.00061
$C_6H_{14}SO_4$	Dipropyl sulfate	0	2	2	1	2	4	0	4	0	0	0	0	0	97.61617	97.609	-0.00008

Table 15.188. The bond angle parameters of alkyl sulfates and experimental values [1]. In the calculation of θ_r, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle O_a S O_b$	2.72654	2.72654	4.7329	-15.95954 O_a	9	-15.95954 O_b	9	0.85252	0.85252	1	1	1	0.85252	-1.65376				120.44	120.9 [44] (dimethyl sulfate)
$\angle O_a S O_c$	2.72654	2.96203	4.6690	-15.95954 O_a	9	-16.11722 O_c	11	0.85252	0.84418	1	1	1	0.84835	-1.65376				110.26	109.67 [44] (dimethyl sulfate)
$\angle O_c S O_d$	2.96203	2.96203	4.6476	-16.11722 O_c	11	-16.11722 O_d	11	0.84418	0.84418	1	1	1	0.84418	-1.65376				103.35	103.85 [44] (dimethyl sulfate)
$\angle C_a O_c S$	2.68862	2.96203	4.8416	-15.75493 C_a	7	-10.36001 S	S	0.86359	0.77641 (Eq. (15.139))	1	0.77641 (Eq. (15.139))	1	0.82000	-0.72457				117.84	117.43[44] (dimethyl sulfate)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_a C_b C_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_a C_b H$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_a C_b C_c$															70.56			109.44	
$\angle C_a C_b H$															70.56			109.44	
$\angle C_b C_a C_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_b C_a H$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_a C_b H$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_b C_a C_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_b C_a C_d$															72.50			107.50	

NITROALKANES ($C_nH_{2n+2-m}(NO_2)_m$, $n=1,2,3,4,5...\infty$)

The nitroalkanes, $C_nH_{2n+2-m}(NO_2)_m$, comprise a NO_2 functional group and a $C-N$ functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The electron configuration of nitrogen is $1s^2 2s^2 2p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state ${}^4S^0_{3/2}$. The bonding in the nitro (NO_2) functional group is similar to that in the SO_2 group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO_2 group, the two unpaired electrons of the O atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the $C2sp^3$ HO. In nitroalkanes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489\,eV$ (Eq. (15.25)), the N AO has an energy of $E(N)=-14.53414\,eV$, and the O AO has an energy of $E(O)=-13.61806\,eV$ [38]. To meet the equipotential condition of the union of the $N=O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $N=O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O\ to\ N2p\ to\ C2sp^3HO) &= \frac{E(O)}{E(N)}c_2(C2sp^3HO) \\ &= \frac{-13.61806\,eV}{-14.53414\,eV}(0.91771) \\ &= 0.85987 \end{aligned} \tag{15.140}$$

Since there are two O atoms in a linear combination that comprises the bonding of the NO_2 group, the unpaired electrons of each O cancel each others effect such that E_{mag} is not subtracted from the total energy of NO_2. Additionally, $E_T\left(atom-atom,msp^3.AO\right)=-3.71673\ eV=4\left(-0.92918\ eV\right)$ (Eq. (14.513)) is the maximum given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The $C-N$ group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and $\Delta E_{H_2MO}\left(AO/HO\right)=-0.72457\ eV$ for nitroalkane and $\Delta E_{H_2MO}\left(AO/HO\right)=-1.44915\ eV$ for primary amines. Whereas, $E_T\left(atom-atom,msp^3.AO\right)=-1.44915\ eV$ for both functional groups. This condition matches the energy of the $C-N$ group with the NO_2 having $\Delta E_{H_2MO}\left(AO/HO\right)=0$.

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each $E_{D(Group)}$ of Table 15.192 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using Eqs. (15.79-15.108) are given in Table 15.194.

Table 15.189. The symbols of functional groups of nitroalkanes.

Functional Group	Group Symbol
NO_2 group	NO_2
C-N	$C-N$
CH_3 group	$C-H\ \left(CH_3\right)$
CH_2 group	$C-H\ \left(CH_2\right)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.190. The geometrical bond parameters of nitroalkanes and experimental values [1].

Parameter	NO_2 Group	$C-N$ Group	$C'-H\ (C'H_3)$ Group	$C'-H\ (C'H_2)$ Group	$C-H$ Group	$C'-C$ (a) Group	$C'-C$ (b) Group	$C-C'$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.33221	1.97794	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.15421	1.40639	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.22157	1.48846	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.224 (nitromethane)	1.489 (nitromethane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.66526	1.39079	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.86639	0.71104	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.191. The MO to HO intercept geometrical bond parameters of nitroalkanes. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C'2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RN(O)=O$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		135.25	44.75	66.05	0.54089	0.61333
$RN(O)=O$	N	-0.92918	-0.92918	-0.72457	0		0.93084	0.78155	-17.40869		131.57	48.43	61.50	0.63558	0.51864
H_3C-NO_2	C'	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	80.47	99.53	38.35	1.55123	0.14484
RH_2C-NO_2 $R=H,alkyl$	N	-0.92918	-0.92918	-0.72457	0		0.93084	0.78155	-17.40869		69.30	110.70	31.71	1.68259	0.27620
$-H_2C_a-NO_2$	C'_a	-0.72457	-0.92918	0	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	74.96	105.04	34.98	1.62061	0.21422
$C'-H\ (C'H_3)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\ (C'H_2)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\ (C'H)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC_bH_2C'H_2-$ $(C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC'_bH_2C'H_2-$ $(C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ $(C'-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)C'H_2-$ $(C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b\left(H_2C'_c-R'\right)HC'H_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC'_a\left(R'-H_2C'_d\right)C'_b\left(R''-H_2C'_e\right)CH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.192. The energy parameters (eV) of functional groups of nitroalkanes.

Parameters	NO_2 Group	$C-N$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	3	2	1	1	1	1	1	1	1
n_2	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85987	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	1	1	0	0	0	1	1	0
c_4	4	2	1	1	1	2	2	2	2	2	2
c_5	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1
V_e (eV)	-106.90919	-31.36351	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.57588	9.67426	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	40.12475	7.92833	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-20.06238	-3.96416	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(no\ ne)$ (eV)	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2NO}(no\ ne)$ (eV)	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(no\ ne)$ (eV)	0	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2no)$ (eV)	-63.27093	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, nsp^3.AO\right)$ (eV)	-3.71673	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(no)$ (eV)	-66.98746	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	19.0113	10.5087	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	12.51354	6.91703	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_p$ (eV)	-0.23440	-0.17214	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Vdw}$ (eV)	0.19342 [45]	0.10539 [45]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{use}$ (eV)	-0.13769	-0.11945	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(tinop)$ (eV)	-67.26284	-33.20397	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(e_1, no\ ne)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(e_1, no\ ne)$ (eV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{fg}(Group)$ (eV)	8.72329	3.93419	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.193. The total bond energies of nitroalkanes calculated using the functional group composition and the energies of Table 15.192 compared to the experimental values [3]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_{fg}(Group)$ (eV) values based on composition is given by (15.58).

Formula	Name	NO_2 Group	$C-N$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Nitromethane	1	1	1	0	0	0	0	0	0	0	0	0	25.14934	25.107	-0.00168
$C_2H_5NO_2$	Nitroethane	1	1	1	1	0	1	0	0	0	0	0	0	37.30704	37.292	-0.00040
$C_3H_7NO_2$	1-Nitropropane	1	1	1	2	0	2	0	0	0	0	0	0	49.46474	49.451	-0.00028
$C_3H_7NO_2$	2-Nitropropane	1	1	2	0	1	0	2	0	0	0	0	0	49.56563	49.602	0.00074
$C_4H_9NO_2$	1-Nitrobutane	1	1	1	3	0	3	0	0	0	0	0	0	61.62244	61.601	-0.00036
$C_4H_9NO_2$	2-Nitroisobutane	1	1	3	0	0	0	0	3	0	0	0	-1	61.90697	61.945	0.00061
$C_5H_{11}NO_2$	1-Nitropentane	1	1	1	4	0	4	0	0	0	0	0	0	73.78014	73.759	-0.00028

Table 15.194. The bond angle parameters of nitroalkanes and experimental values [1]. In the calculation of $\theta_{e,}$ the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle NC_aH$	2.81279	2.09711	3.9665	-14.82575	1	-14.53414	N	0.91771	0.91140 (Eq. (15.116))	0.75	1	0.75	0.99312	0				106.87	107 (nitromethane)
$\angle O_aNO_b$	2.30843	2.30843	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				126.52	125.3 (nitromethane)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL NITRITES ($C_nH_{2n+2-m}\left(NO_2\right)_m$, $n=1,2,3,4,5...\infty$)

The alkyl nitrites, $C_nH_{2n+2-m}\left(NO_2\right)_m$, comprise a $RC-O-NO$ moiety that comprises $C-O$, $O-N$, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state ${}^4S^0_{3/2}$. The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the $O-N$ functional group that is further energy matched to the $C2sp^3$ HO of the $C-O$ functional group. To meet the equipotential condition of the union of the $N=O$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $N=O$-bond MO given by Eq. (15.140) is $c_2\left(O\ to\ N2p\ to\ C2sp^3HO\right)=0.85987$.

As in the case of the carbonyl group, two unpaired O electrons result upon bond breakage of the $N=O$ bond which requires that two times E_{mag} of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally, $E_T\left(atom-atom,msp^3.AO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ are equal to $-0.92918\ eV$ (Eq. (14.513)) which matches the energy of the $N=O$ bond with the contiguous $O-N$ bond and matches the energy contribution of an oxygen atom.

The $O-N$ functional group comprise a single-bond, H_2-type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the $C-O$ functional group. In alkyl nitrites, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eq. (15.114) is $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$. The hybridization factor c_2 of Eq. (15.52) for a $C-N$-bond MO given by Eq. (15.116) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$. Thus, the hybridization factor c_2 of Eq. (15.52) for $O-N$ that bridges the $C-O$ and $N=O$ bonds given by Eq. (15.69) is

$$c_2\left(N2p\ to\ O2p\right)=\frac{c_2\left(C2sp^3HO\ to\ N\right)}{c_2\left(C2sp^3HO\ to\ O\right)}=\frac{0.91140}{0.85395}=1.06727 \tag{15.141}$$

$E_T\left(atom-atom,msp^3.AO\right)=-0.92918\ eV$ in order to match the energy of the NO group and $E\left(AO/HO\right)=-15.35946\ eV$ in order to match the $C-O$ functional group.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T\left(atom-atom,msp^3.AO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ are both $-0.72457\ eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15.195. The symbols of functional groups of alkyl nitrites.

Functional Group	Group Symbol
NO group	*NO*
O-N	*O–N*
C-O	*C–O*
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	*C–H*
CC bond (n-C)	*C'–C'* (a)
CC bond (iso-C)	*C'–C'* (b)
CC bond (tert-C)	*C'–C'* (c)
CC (iso to iso-C)	*C'–C'* (d)
CC (t to t-C)	*C'–C'* (e)
CC (t to iso-C)	*C'–C'* (f)

Table 15.196. The geometrical bond parameters of alkyl nitrites and experimental values [1].

Parameter	*NO* Group	*O–N* Group	*C–O* Group	*C–H* (CH_3) Group	*C–H* (CH_2) Group	*C–H* Group	*C–C* (a) Group	*C–C* (b) Group	*C–C* (c) Group	*C–C* (d) Group	*C–C* (e) Group	*C–C* (f) Group
$a\ (a_0)$	1.32255	1.76440	1.85327	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_n)$	1.15002	1.32831	1.36135	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\text{Å})$	1.21713	1.40582	1.44079	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.205 (methyl nitrate) 1.2 (HNO_2)	1.402 (methyl nitrate) 1.432 (HNO_2)	1.437 (methyl nitrate)	1.107 (*C–H* propane) 1.117 (*C–H* butane)	1.107 (*C–H* propane) 1.117 (*C–H* butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.65314	1.16134	1.25751	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.86955	0.75284	0.73457	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nitrites. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RON=O$	O	-0.46459	0	0	0		1.00000	0.88983	-15.29034		137.15	42.85	67.90	0.49764	0.65238
$RON=O$	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		136.09	43.91	66.48	0.52781	0.62221
RO_b-NO_a	O_b	-0.46459	-0.36229	0	0		1.00000	0.86923	-15.65263		99.22	80.78	47.63	1.18905	0.13925
RO_b-NO_a	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		98.78	81.22	47.30	1.19655	0.13175
$RH_2C_a-O_bNO_a$ $R=H,alkyl$	O_b	-0.36229	-0.46459	0	0		1.00000	0.86923	-15.65263		91.43	88.57	43.71	1.33962	0.02173
$H_3C_a-O_bNO_a$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	93.71	86.29	45.31	1.30342	0.05793
$-CH_2H_2C_a-O_bNO_a$	C_a	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	89.16	90.84	42.16	1.37373	0.01238
$C-H\ (CH_3)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\ (CH_2)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\ (CH)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_e\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.198. The energy parameters (eV) of functional groups of alkyl nitrites.

Parameters	NO Group	$O-N$ Group	$C-O$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1^*	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2^*	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	0	0	0	1	1	0	0	0	1	1	0
c_4	4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1n}^*	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2n}^*	1	1	1	1	1	1	1	1	1	1	1	1
V_c (eV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.66182	20.48593	9.99436	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	40.95920	12.13739	8.64465	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ne} (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(no\ nn)$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{tt,NO}(no\ nn)$ (eV)	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(no\ nn)$ (eV)	0.92918	-15.35946	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(tt_2 nn)$ (eV)	-63.27057	-31.63527	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom, nsp^3, AO\right)$ (eV)	-0.92918	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(nn)$ (eV)	-64.19992	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	19.2199	23.3578	20.7301	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	12.65089	15.37450	13.64490	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{J1}$ (eV)	-0.22587	0.25261	-0.23648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Krab}$ (eV)	0.20396 [46]	0.10725 [47]	0.13663 [21]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{ne2}$ (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{neng} (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(cnorg)$ (eV)	-64.44771	32.76354	-32.52811	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{mtneg}(e_s, no\ nn)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{mtneg}(e_s, no\ nn)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{J1}(cnorg)$ (eV)	5.67933	3.49376	3.25833	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.199. The total bond energies of alkyl nitrites calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula	Name	NO Group	$O-N$ Group	$C-O$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Methyl nitrite	1	1	1	1	0	0	0	0	0	0	0	0	24.92328	24.955	0.00126

Table 15.200. The bond angle parameters of alkyl nitrites and experimental values [1]. In the calculation of θ_r, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CO_bN$	2.72270	2.65661	4.4944	-16.68412 C_b	25	-14.53414 N	N	0.81549	0.91140 (Eq. (15.116))	1	1	1	0.86345	-1.44915				113.33	
$\angle O_aNO_b$	2.30004	2.65661	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				112.38	110.7 (HNO_2)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL NITRITES ($C_nH_{2n+2-m}\left(NO_2\right)_m$, $n=1,2,3,4,5...\infty$)

The alkyl nitrites, $C_nH_{2n+2-m}\left(NO_2\right)_m$, comprise a $RC-O-NO$ moiety that comprises $C-O$, $O-N$, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($\left(CH_3\right)_2CH$) and t-butyl ($\left(CH_3\right)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state ${}^3P_2$. The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has three unpaired electrons corresponding to the ground state ${}^4S^0_{3/2}$. The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the $O-N$ functional group that is further energy matched to the $C2sp^3$ HO of the $C-O$ functional group. To meet the equipotential condition of the union of the $N=O$ H_2-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the $N=O$-bond MO given by Eq. (15.140) is $c_2\left(O\ to\ N2p\ to\ C2sp^3HO\right)=0.85987$.

As in the case of the carbonyl group, two unpaired O electrons result upon bond breakage of the $N=O$ bond which requires that two times E_{mag} of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally, $E_T\left(atom-atom,msp^3.AO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ are equal to $-0.92918\,eV$ (Eq. (14.513)) which matches the energy of the $N=O$ bond with the contiguous $O-N$ bond and matches the energy contribution of an oxygen atom.

The $O-N$ functional group comprise a single-bond, H_2-type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the $C-O$ functional group. In alkyl nitrites, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eq. (15.114) is $c_2\left(C2sp^3HO\ to\ O\right)=0.85395$. The hybridization factor c_2 of Eq. (15.52) for a $C-N$-bond MO given by Eq. (15.116) is $c_2\left(C2sp^3HO\ to\ N\right)=0.91140$. Thus, the hybridization factor c_2 of Eq. (15.52) for $O-N$ that bridges the $C-O$ and $N=O$ bonds given by Eq. (15.69) is

$$c_2\left(N2p\ to\ O2p\right)=\frac{c_2\left(C2sp^3HO\ to\ N\right)}{c_2\left(C2sp^3HO\ to\ O\right)}=\frac{0.91140}{0.85395}=1.06727 \tag{15.141}$$

$E_T\left(atom-atom,msp^3.AO\right)=-0.92918\ eV$ in order to match the energy of the NO group and $E\left(AO/HO\right)=-15.35946\ eV$ in order to match the $C-O$ functional group.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T\left(atom-atom,msp^3.AO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ are both $-0.72457\ eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15.195. The symbols of functional groups of alkyl nitrites.

Functional Group	Group Symbol
NO group	*NO*
O-N	*O–N*
C-O	*C–O*
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	*C–H*
CC bond (*n*-C)	*C–C* (a)
CC bond (iso-C)	*C–C* (b)
CC bond (tert-C)	*C–C* (c)
CC (iso to iso-C)	*C–C* (d)
CC (*t* to *t*-C)	*C–C* (e)
CC (t to iso-C)	*C–C* (f)

Table 15.196. The geometrical bond parameters of alkyl nitrites and experimental values [1].

Parameter	*NO* Group	*O–N* Group	*C–O* Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	*C–H* Group	*C–C* (a) Group	*C–C* (b) Group	*C–C* (c) Group	*C–C* (d) Group	*C–C* (e) Group	*C–C* (f) Group
$a\ (a_0)$	1.32255	1.76440	1.85327	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.15002	1.32831	1.36135	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\text{Å})$	1.21713	1.40582	1.44079	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length (Å)	1.205 (methyl nitrate) 1.2 (HNO_2)	1.402 (methyl nitrate) 1.432 (HNO_2)	1.437 (methyl nitrate)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$b,c\ (a_0)$	0.65314	1.16134	1.25751	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.86955	0.75284	0.73457	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nitrites. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RON=O$	O	-0.46459	0	0	0		1.00000	0.88983	-15.29034		137.15	42.85	67.90	0.49764	0.65238
$RON=O$	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		136.09	43.91	66.48	0.52781	0.62221
RO_h-NO_a	O_h	-0.46459	-0.36229	0	0		1.00000	0.86923	-15.65263		99.22	80.78	47.63	1.18905	0.13925
RO_h-NO_a	N	-0.46459	-0.46459	0	0		0.93084	0.86359	-15.75493		98.78	81.22	47.30	1.19655	0.13175
$RH_2C_a-O_hNO_a$ $R=H,alkyl$	O_h	-0.36229	-0.46459	0	0		1.00000	0.86923	-15.65265		91.43	88.57	43.71	1.33962	0.02173
$H_3C_a-O_hNO_a$	C_a	-0.36229	0	0	0	-151.97798	0.91771	0.89582	-15.18804	-14.99717	93.71	86.29	45.31	1.30342	0.05793
$-CH_2H_2C_a-O_hNO_a$	C_a	-0.36229	-0.92918	0	0	-152.90716	0.91771	0.84418	-16.11722	-15.92636	89.16	90.84	42.16	1.37373	0.01238
$C-H\left(CH_3\right)$	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H\left(CH_2\right)$	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H\left(CH\right)$	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C_aC_bH_2CH_2-$ $(C-C$ (a))	C_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (b))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (c))	C_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (d))	C_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (e))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC_aC_b\left(H_2C_c-R'\right)HCH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C-C$ (f))	C_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.198. The energy parameters (eV) of functional groups of alkyl nitrites.

Parameters	NO Group	$O-N$ Group	$C-O$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	2	0	0	0	1	1	0	0	0	1	1	0
c_4	4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1n}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2n}	1	1	1	1	1	1	1	1	1	1	1	1
V_c (eV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.66182	20.48593	9.99436	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	40.95920	12.13739	8.64465	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_m (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(no\ no)$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{no\ no}(no\ no)$ (eV)	-0.92918	0	-0.72457	0	0	0	0	0	0	0	0	0
$E_T(no\ no)$ (eV)	0.92918	-15.35946	-13.91032	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(n_2no)$ (eV)	-63.27057	-31.63527	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T\left(atom-atom,msp^3,AO\right)$ (eV)	-0.92918	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(no)$ (eV)	-64.19992	-32.56455	-32.35994	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	19.2199	23.3578	20.7301	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_S (eV)	12.65089	15.37450	13.64490	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_D$ (eV)	-0.22587	0.25261	-0.23648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Keesom}$ (eV)	0.20396 [46]	0.10725 [47]	0.13663 [21]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{osc}$ (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{mag} (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-64.44771	32.76354	-32.52811	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(e_4\ no\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(e_5\ no\ no)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_D(Group)$ (eV)	5.67933	3.49376	3.25833	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.199. The total bond energies of alkyl nitrites calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

Formula	Name	NO Group	$O-N$ Group	$C-O$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_2	Methyl nitrite	1	1	1	1	0	0	0	0	0	0	0	0	24.92328	24.955	0.00126

Table 15.200. The bond angle parameters of alkyl nitrites and experimental values [1]. In the calculation of θ_e, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3\text{-}AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CO_bN$	2.72270	2.65661	4.4944	-16.68412 C_b	25	-14.53414 N	N	0.81549	0.91140 (Eq. (15.116))	1	1	1	0.86345	-1.44915				113.33	
$\angle O_aNO_b$	2.30004	2.65661	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				112.38	110.7 (HNO_3)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

ALKYL NITRATES ($C_nH_{2n+2-m}(NO_2)_m$, $n=1,2,3,4,5...\infty$)

The alkyl nitrates, $C_nH_{2n+2-m}(NO_3)_m$, comprise a $RC-O-NO_2$ moiety that comprises $C-O$, $O-N$, and NO_2 functional groups. The alkyl portion of the alkyl nitrate may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of $C-C$ bonds can be identified. The n-alkane $C-C$ bond is the same as that of straight-chain alkanes. In addition, the $C-C$ bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl $C-C$ bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The NO_2 functional group is equivalent to that of nitro alkanes with the exception that $\Delta E_{H_2MO}(AO/HO)$ as well as $E_T(atom-atom,msp^3.AO)$ is equal to $-3.71673\,eV$ in order to match the group energy to that of the contiguous $O-N$ bond. Furthermore, the $O-N$ group with $E_T(atom-atom,msp^3.AO)=-0.92918\,eV$ is equivalent to that of nitrites as given in the corresponding section.

The $C-O$ functional group is equivalent to that of an ether as given in the corresponding section except that $E_T(atom-atom,msp^3.AO)$ and $\Delta E_{H_2MO}(AO/HO)$ are both $-0.92918\,eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.79-15.108) are given in Table 15.206.

Table 15.201. The symbols of functional groups of alkyl nitrates.

Functional Group	Group Symbol
NO_2 group	NO_2
O-N	$O-N$
C-O	$C-O$
CH_3 group	$C-H\ (CH_3)$
CH_2 group	$C-H\ (CH_2)$
CH	$C-H$
CC bond (n-C)	$C-C$ (a)
CC bond (iso-C)	$C-C$ (b)
CC bond (tert-C)	$C-C$ (c)
CC (iso to iso-C)	$C-C$ (d)
CC (t to t-C)	$C-C$ (e)
CC (t to iso-C)	$C-C$ (f)

Table 15.202. The geometrical bond parameters of alkyl nitrates and experimental values [1].

Parameter	NO_2 Group	$O-N$ Group	$C-O$ Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
$a\ (a_0)$	1.29538	1.76440	1.83991	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'\ (a_0)$	1.13815	1.32831	1.35643	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length $2c'\ (\AA)$	1.20456	1.40582	1.43559	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond Length $(\AA)$	1.205 (methyl nitrate) 1.2 (HNO_2)	1.402 (methyl nitrate) 1.432 (HNO_2)	1.437 (methyl nitrate)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
$h,c\ (a_0)$	0.61857	1.16134	1.24312	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
e	0.87862	0.75284	0.73723	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.203. The MO to HO intercept geometrical bond parameters of alkyl nitrates. R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, nsp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	r_{mutual} (a_0)	r_{final} (a_0)	$E_{Coulomb}$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$RN(O)=O$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		138.49	41.51	67.70	0.49144	0.64671
$RN(O)=O$	N	-0.92918	-0.92918	-0.46459	0		0.93084	0.79340	-17.14870		135.60	44.40	63.83	0.57133	0.56682
$RO_b-N(O_a)_2$	O_b	-0.46459	-0.46459	0	0		1.00000	0.86359	-15.75493		98.78	81.22	47.30	1.19655	0.13175
$RO_b-N(O_a)_2$	N	-0.46459	-0.92918	-0.92918	0		0.93084	0.79340	-17.14870		92.78	87.22	43.03	1.28978	0.03852
$RH_2C_a-O_bN(O_a)_2$ $R=H, alkyl$	O_b	-0.46459	-0.46459	0	0		1.00000	0.86359	-15.75493		92.13	87.87	43.96	1.32431	0.05212
$H_3C_a-O_bN(O_a)_2$	C'_a	-0.46459	0	0	0	-152.08028	0.91771	0.88983	-15.29034	-15.09948	94.36	85.64	45.54	1.28872	0.06771
$-CH_2H_2C_a-O_bN(O_a)_2$	C'_a	-0.46459	-0.92918	0	0	-153.00946	0.91771	0.83885	-16.21952	-16.02866	89.90	90.10	42.44	1.35787	0.00143
$C'-H\left(C'H_3\right)$	C'	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C'-H\left(C'H_2\right)$	C'	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C'-H\left(C'H\right)$	C'	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
$H_3C'_aC'_bH_2CH_2-$ $(C'-C'$ (a))	C'_a	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
$H_3C'_aC'_bH_2C'H_2-$ $(C'-C'$ (a))	C'_b	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_2C_aC_b\left(H_2C_c-R'\right)HC'H_2-$ $(C'-C'$ (b))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$R-H_2C_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)C'H_2-$ $(C-C'$ (c))	C'_b	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	-17.92866	-17.73779	48.21	131.79	21.74	1.95734	0.50570
$isoC_aC_b\left(H_2C_c-R'\right)HC'H_2-$ $(C'-C'$ (d))	C'_b	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.51388
$tertC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)C'H_2-$ $(C'-C'$ (e))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298
$tertC'_aC'_b\left(H_2C_c-R'\right)HC'H_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.92918	-0.92918	0-	-154.19863	0.91771	0.78155	-17.40869	-17.21783	52.78	127.22	24.04	1.92443	0.47279
$isoC_a\left(R'-H_2C_d\right)C_b\left(R''-H_2C_c\right)CH_2-$ $(C'-C'$ (f))	C'_b	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.204. The energy parameters (eV) of functional groups of alkyl nitrates.

Parameters	NO_2 Group	$O-N$ Group	$C-O$ Group	CH_3 Group	CH_2 Group	$C-H$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-C$ (f) Group
n_1	2	1	1	3	2	1	1	1	1	1	1	1
n_2	0	0	0	2	1	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_2	1	1	1	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1	1	1
c_2	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	0	1	1	0	0	0	1	1	0
c_4	4	2	2	1	1	1	2	2	2	2	2	2
c_5	0	0	0	3	2	1	0	0	0	0	0	0
C_{1o}	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C_{2o}	1	1	1	1	1	1	1	1	1	1	1	1
V_r (eV)	-112.63415	-42.83043	-32.35681	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V_p (eV)	23.90868	20.48593	10.03058	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	43.47534	12.13739	8.79304	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_{ne} (eV)	-21.73767	-6.06870	-4.39652	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
$E(\omega no)$ (eV)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_2NO}(\omega no)$ (eV)	-3.71673	0	-0.92918	0	0	0	0	0	0	0	0	0
$E_T(\omega no)$ (eV)	3.71673	-15.35946	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H_2\omega)$ (eV)	-63.27107	-31.63527	-31.63542	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom-atom, msp^3.AO)$ (eV)	-3.71673	-0.92918	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_T(\omega)$ (eV)	-66.98746	-32.56455	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega\left(10^{15}\ rad/s\right)$	19.8278	23.3578	21.0910	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_K (eV)	13.05099	15.37450	13.88249	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\overline{E}_{ij}$ (eV)	-0.23938	0.25261	-0.24004	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\overline{E}_{Kroh}$ (eV)	0.19342 [45]	0.10725 [47]	0.13663 [21]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
$\overline{E}_{exc}$ (eV)	-0.14267	0.19899	-0.17172	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_{exc} (eV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(virial)$ (eV)	-67.27281	32.76354	-32.73627	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
$E_{united}(\varepsilon_i, \omega no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{united}(\varepsilon_i, \omega no)$ (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{ij}(virial)$ (eV)	8.73325	3.49376	3.46649	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.205. The total bond energies of alkyl nitrates calculated using the functional group composition and the energies of Table 15.204 compared to the experimental values [3].

Formula	Name	NO_2 Group	$O-N$ Group	$C-O$ Group	CH_3	CH_2	CH	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	$C-C$ (f)	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_3	Methyl nitrate	1	1	1	1	0	0	0	0	0	0	0	0	28.18536	28.117	-0.00244
$C_2H_5NO_3$	Ethyl nitrate	1	1	1	1	1	0	1	0	0	0	0	0	40.34306	40.396	0.00131
$C_3H_7NO_3$	Propyl nitrate	1	1	1	1	2	1	2	0	0	0	0	0	52.50076	52.550	0.00093
$C_3H_7NO_3$	Isopropyl nitrate	1	1	1	2	0	1	0	2	0	0	0	0	52.60165	52.725	0.00233

Table 15.206. The bond angle parameters of alkyl nitrates and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c^1$ Bond 1 (a_0)	$2c^1$ Bond 2 (a_0)	$2c^1$ Terminal Atoms (a_0)	$E_{Coulombic}$ or E Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle H_aC_aO_c$															70.56			109.44	110 (methyl nitrate)
$\angle H_bC_aO_c$	2.09711	2.71287	3.7238	-14.82575 C_a	1	-13.61806	O	0.91771	0.85395 (Eq. (15.114))	0.75	1	0.75	0.93052	0				100.68	103 (methyl nitrate)
$\angle O_aNO_b$	2.27630	2.27630	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				129.83	
$\angle O_aNO_c$																129.83		115.09 (Eq. (15.99))	118.1 (methyl nitrate)
$\angle O_bNO_c$																129.83		115.09 (Eq. (15.99))	112.4 (methyl nitrate)
$\angle CO_cN$	2.71287	2.65661	4.4721	-16.68412 C_b	25	-14.53414 N	N	0.81549	0.91140 (Eq. (15.116))	1	1	1	0.86345	-1.44915				112.79	112.7 (methyl nitrate)
Methylene $\angle HC_aH$	2.11106	2.11106	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				108.44	107 (propane)
$\angle C_aC_bC_c$															69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
$\angle C_aC_bH$															69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl $\angle HC_aH$	2.09711	2.09711	3.4252	-15.75493	7	H	H	0.86359	1	1	1	0.75	1.15796	0				109.50	
$\angle C_aC_bC_c$															70.56			109.44	
$\angle C_aC_bH$															70.56			109.44	
$\angle C_bC_aC_c$ iso C_a	2.91547	2.91547	4.7958	-16.68412 C_b	25	-16.68412 C_c	25	0.81549	0.81549	1	1	1	0.81549	-1.85836				110.67	110.8 (isobutane)
$\angle C_bC_aH$ iso C_a	2.91547	2.11323	4.1633	-15.55033 C_a	5	-14.82575 C_b	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				110.76	
$\angle C_aC_bH$ iso C_a	2.91547	2.09711	4.1633	-15.55033 C_b	5	-14.82575 C_a	1	0.87495	0.91771	0.75	1	0.75	1.04887	0				111.27	111.4 (isobutane)
$\angle C_bC_aC_c$ tert C_a	2.90327	2.90327	4.7958	-15.55033 C_b	5	-14.82575 C_c	1	0.87495	0.91771	0.75	1	0.75	1.04887	-1.85836				111.27	111.4 (isobutane)
$\angle C_bC_aC_d$															72.50			107.50	

CYCLIC AND CONJUGATED ALKENES

($C_nH_{2n+2-2m-2c}$, $n=3,4,5...\infty$, $m=1,2,3...$, $c=0$ *or* 1)

The cyclic and conjugated alkenes are represented by the general formula $C_nH_{2n+2-2m-2c}$, $n=3,4,5...\infty$, $m=1,2,3...$, $c=0$ *or* 1 where m is the number of double bonds and $c=0$ for a straight-chain alkene and $c=1$ for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, five distinct $C-C$ functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 61A-E. In addition, CH_2 of any $-C=CH_2$ moiety is an conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group (CH_3), and may comprise methylene (CH_2), and methylyne (CH) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The $C-C$ groups are solved in the same manner as those of the branched-chain alkanes given in the corresponding section. For example, the cyclopentene C_a-C_b group is equivalent to the n-$C-C$ alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of H from the terminal methyl and methylene groups. Thus, the energy of each of the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene C_c-C_d and the cyclopentadiene C_a-C_b groups is the magnetic energy (Eq. (15.58)) which is subtracted from the C_a-C_b total bond energy according to Eqs. (13.524-13.527) due to the formation of a CH group from the methylene group.

$E_T\left(atom-atom, msp^3.AO\right)$ of the $C=C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, –2.26759 eV, given by

Eq. (14.247). $E_T\left(atom-atom,msp^3.AO\right)$ of each $C-C$-bond MO in Eq. (15.52) is $-2.26759\,eV$ or $-1.85836\,eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of alkene, $-1.13379\,eV$ (Eq. (14.247)), or methylene, $-0.92918\,eV$ (Eq. (14.513)), groups, respectively, that are contiguous with the $C-C$-bond carbons. In the former case, the total energy of the $C-C$ bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of 0.5e must be donated to the $C-C$ bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the $C-C$-bond MO and increases the $C-C$ bond energy. This additional lowering of the $C-C$-bond energy by additional charge donation over that of an alkane bond due to adjacent double bonds is called *conjugation.*

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 61A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.79-15.108) are given in Table 15.212.

Table 15.207. The symbols of functional groups of cyclic and conjugated alkenes.

Functional Group	Group Symbol
CC double bond	$C=C$
1,3-butadiene, 1,3-pentadiene C_b-C_b 1,3-cyclopentadiene C_c-C_c	$C-C$ (a)
1,3-pentadiene C_c-C_d cyclopentene C_b-C_c	$C-C$ (b)
1,4-pentadiene C_b-C_e	$C-C$ (c)
1,3-cyclopentadiene C_a-C_b	$C-C$ (d)
cyclopentene C_a-C_b	$C-C$ (e)
CH_2 alkenyl group	$C-H\ (CH_2)$ (i)
CH_3 group	$C-H\ (CH_3)$
CH_2 alkyl group	$C-H\ (CH_2)$ (ii)
CH	$C-H$

Table 15.208. The geometrical bond parameters of cyclic and conjugated alkenes and experimental values [1].

Parameter	$C=C$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	$C-H\ (CH_2)$ (i) Group	$C-H\ (CH_3)$ Group	$C-H\ (CH_2)$ (ii) Group	$C-H$ Group
$a\ (a_0)$	1.47228	1.91256	2.04740	2.04740	2.04740	2.12499	1.64010	1.64920	1.67122	1.67465
$c'\ (a_0)$	1.26661	1.38295	1.43087	1.43087	1.43087	1.45773	1.04566	1.04856	1.05553	1.05661
Bond Length $2c'\ (\text{Å})$	1.34052	1.46365	1.51437	1.51437	1.51437	1.54280	1.10668	1.10974	1.11713	1.11827
Exp. Bond Length (Å)	1.349 (1,3-butadiene) 1.342 (1,3-cyclopentadiene) 1.342 (cyclopentene)	1.467 (1,3-butadiene) 1.469 (1,3-cyclopentadiene)	1.519 (cyclopentene)		1.509 (1,3-cyclopentadiene)	1.546 (cyclopentene)	1.10 (2-methylpropene) 1.108 (avg.) (1,3-butadiene)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.107 ($C-H$ propane) 1.117 ($C-H$ butane)	1.122 (isobutane)
$b,c\ (a_0)$	0.75055	1.32110	1.46439	1.46439	1.46439	1.54615	1.26354	1.27295	1.29569	1.29924
e	0.86030	0.72309	0.69887	0.69887	0.69887	0.68600	0.63756	0.63580	0.63159	0.63095

Table 15.209. The MO to HO intercept geometrical bond parameters of cyclic and conjugated alkenes R_1 is an alkyl group and R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{rotated}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$H_2C_a=C_b(H)(H)C=CR$ (1,3-butadiene, 1,3-pentadiene) $H_2C_a=C_b(H)C_cH_2C_b(H)=C_aH_2$ (1,4-pentadiene)	C_a	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	129.84	50.16	60.70	0.72040	0.54620
$H_2C_a=C_b(H)(H)C=CR$ (1,3-butadiene, 1,3-pentadiene) $-HC_b=C_c(H)(H)C_c=C_bH-$ (1,3-cyclopentadiene)	C_b C_c	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	127.13	52.87	57.73	0.78613	0.48047
$H_2C_a=C_b(H)(H)C_b=C_c(H)C_dH_3$ (1,3-pentadiene) $H_2C_a=C_b(H)C_cH_2C_b(H)=C_aH_2$ (1,4-pentadiene) $-HC_b=C_c(H)(H)C_c=C_bH-$ (1,3-cyclopentadiene) $-H_2C_bC_c(H)=(H)C_cC_bH_2-$ (cyclopentene)	C_c C_b C_c C_c	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	0.49168
$RC=C_{b,c}(H)-(H)C_{b,c}=CR'$ ($C-C$ (a))	$C_{b,c}$	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	78.31	101.69	36.16	1.54418	0.16123
$H_2C_a=C_b(H)(H)C_b=C_c(H)-C_dH_3$ (1,3-pentadiene) $-H_2C_b-C_c(H)=(H)C_c-C_bH_2-$ (cyclopentene) ($C-C$ (b))	C_c C_c	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$H_2C_a=C_b(H)(H)C_b=C_c(H)-C_dH_3$ (1,3-pentadiene) ($C-C$ (b))	C_d	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	72.27	107.73	34.17	1.69388	0.26301
$-H_2C_b-C_c(H)=(H)C_c-C_bH_2-$ (cyclopentene) ($C-C$ (b))	C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$H_2C_a=C_b(H)-C_cH_2C_b(H)=C_aH_2$ (1,4-pentadiene) ($C-C$ (c)) $-H_2C_a-HC_b=C_c(H)(H)C_c=C_bH-$ (1,3-cyclopentadiene) ($C-C$ (d))	C_b C_b	-1.13380	-0.92918	0	0	-153.67866	0.91771	0.80561	-16.88873	-16.69786	64.57	115.43	29.79	1.77684	0.34596
$H_2C_a=C_b(H)-C_cH_2C_b(H)=C_aH_2$ (1,4-pentadiene) ($C-C$ (c)) $-H_2C_a-HC_b=C_c(H)(H)C_c=C_bH-$ (1,3-cyclopentadiene) ($C-C$ (d))	C_c C_a	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0.33183
$-H_2C_a-H_2C_bC_c(H)=(H)C_cC_bH_2-$ (cyclopentene) ($C-C$ (e))	C_a, C_b	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	56.41	123.59	26.06	1.90890	0.45116
$C-H$ (CH_2) (i)	C	-1.13380	0	0	0	-152.74949	0.91771	0.85252	-15.95955	-15.76868	77.15	102.85	41.13	1.23531	0.18965
$C-H$ (CH_3)	C	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ (CH_2) (ii)	C	-0.92918	-0.92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
$C-H$ (CH)	C	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326

Table 15.210. The energy parameters (eV) of functional groups of cyclic and conjugated alkenes.

Parameters	$C=C$ Group	$C-C$ (a) Group	$C-C$ (b) Group	$C-C$ (c) Group	$C-C$ (d) Group	$C-C$ (e) Group	CH_2 (i) Group	CH_3 Group	CH_2 (ii) Group	$C-H$ Group
n_1	2	1	1	1	1	1	2	3	2	1
n_2	0	0	0	0	0	0	1	2	1	0
n_3	0	0	0	0	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75
C_2	0.91771	1	1	1	1	1	1	1	1	1
c_1	1	1	1	1	1	1	1	1	1	1
c_2	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771
c_3	0	0	0	0	1	0	1	0	1	1
c_4	4	2	2	2	2	2	1	1	1	1
c_5	0	0	0	0	0	0	2	3	2	1
$C_{1\pi}$	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75
$C_{2\pi}$	0.91771	1	1	1	1	1	1	1	1	1
V_e (eV)	-102.08992	-33.01226	-30.19634	-30.19634	-30.19634	-28.79214	-72.03287	-107.32728	-70.41425	-35.12015
V_p (eV)	21.48386	9.83824	9.50874	9.50874	9.50874	9.33352	26.02344	38.92728	25.78002	12.87680
T (eV)	34.67062	8.63041	7.37432	7.37432	7.37432	6.77464	21.95990	32.53914	21.06675	10.48582
V_m (eV)	-17.33531	-4.31520	-3.68716	-3.68716	-3.68716	-3.38732	-10.97995	-16.26957	-10.53337	-5.24291
$E(\pi\,no)$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
$\Delta E_{H_2MO}(\pi\,no)$ (eV)	0	-1.85836	0	0	0	0	0	0	0	0
$E_T(\pi\,no)$ (eV)	0	-12.77653	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
$E_T(\pi_2 no)$ (eV)	-63.27075	-31.63535	-31.63534	-31.63534	-31.63534	-31.63537	-49.66437	-67.69451	-49.66493	-31.63533
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	-2.26759	-2.26759	-1.85836	-1.85836	-1.85836	-1.85836	0	0	0	0
$E_T(\sigma o)$ (eV)	-65.53833	-33.90295	-33.49373	-33.49373	-33.49373	-33.49373	-49.66493	-67.69450	-49.66493	-31.63537
$\omega\left(10^{15}\ rad/s\right)$	43.0680	11.0522	9.97851	23.3291	9.97851	9.43699	25.2077	24.9286	24.2751	24.1759
E_K (eV)	28.34813	7.27475	6.56803	15.35563	6.56803	6.21159	16.59214	16.40846	15.97831	15.91299
$\bar{E}_D$ (eV)	-0.34517	-0.18090	-0.16982	-0.25966	-0.16982	-0.16515	-0.25493	-0.25352	-0.25017	-0.24966
$\bar{E}_{AVib}$ (eV)	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.11159 [12]	0.11159 [12]	0.12312 [2]	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)
$\bar{E}_{mc}$ (eV)	-0.25568	-0.10676	-0.11402	-0.20386	-0.11402	-0.10359	-0.07727	-0.22757	-0.14502	-0.07200
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(group)$ (eV)	-66.04969	-34.00972	-33.60776	-33.69760	-33.60776	-33.59732	-49.81948	-67.92207	-49.80996	-31.70737
$E_{initial}(\sigma_1 no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(\sigma_2 no)$ (eV)	0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844
$E_D(group)$ (eV)	7.51014	4.73994	4.33798	4.42782	4.18995	4.32754	7.83968	12.49186	7.83016	3.32601

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(group)$ (eV) values based on composition is given by (15.58).

Formula	Name	$C=C$	$C-C$ (a)	$C-C$ (b)	$C-C$ (c)	$C-C$ (d)	$C-C$ (e)	CH_2 (i)	CH_3	CH_2 (ii)	CH	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_6	1,3 Butadiene	2	1	0	0	0	0	2	0	0	2	0	42.09159	42.12705	0.00084
C_5H_8	1,3 Pentadiene	2	1	1	0	0	0	1	1	0	0	0	54.40776	54.42484	0.00031
C_5H_8	1,4 Pentadiene	2	0	0	2	0	0	2	0	1	2	0	54.03745	54.11806	0.00149
C_5H_6	1,3 Cyclopentadiene	2	1	0	0	2	0	0	0	1	4	0	49.27432	49.30294	0.00058
C_5H_8	Cyclopentene	1	0	2	0	0	2	0	0	3	2	-1	54.83565	54.86117	0.00047

Table 15.212. The bond angle parameters of cyclic and conjugated alkenes and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aH$ $H_2C_a=C_b$ 1,3-butadiene	2.09132	2.09132	3.4928	-15.95955	9	H	H	0.85252	1	1	1	0.75	1.17300	0				113.25	
$\angle C_bC_aH_a$ $H_2C_a=C_b$ 1,3-butadiene																113.25		123.38	120.9 (1,3-butadiene)
$\angle C_bC_aH_a$ $H_2C_a=C_b$ 1,3-butadiene	2.53321	2.09132	4.0000	-15.95954 C_a	9	-15.95954 C_b	9	0.85252	0.85252	0.75	1	0.75	1.00000	0				119.45	120.9 (1,3-butadiene)
$\angle C_aC_bC_b$ $C_a=C_bC_b$ 1,3-butadiene	2.53321	2.76590	4.6904	-16.88873 C_a	27	-17.09334 C_b	30	0.80561	0.79597	1	1	1	0.85395	-1.85836				124.48	124.4 (1,3-butadiene CCC) 124.4 (1,3,5-hexatriene CbCcCc) 121.7 (1,3,5-hexatriene CaCbCc) 125.3 (2-butene CbCaCc)
$\angle C_bC_cC_c$ $C_b=C_cC_c$ 1,3-cyclopentadiene	2.53321	2.76590	4.3012	-17.81791 C_b	46	-17.81791 C_c	46	0.76360	0.76360	1	1	1	0.76360	-1.85836				108.44	109.4 (1,3-cyclopentadiene)
$\angle C_aC_bC_c$ $C_aC_b=C_c$ 1,3-cyclopentadiene	2.86175	2.53321	4.3818	-17.61330 C_a	42	-17.61330 C_c	42	0.77247	0.77247	1	1	1	0.77247	-1.85836				108.47	109.3 (1,3-cyclopentadiene)
$\angle C_bC_aC_b$ $=C_bHC_aH_2C_b\left(H\right)=$ 1,3-cyclopentadiene	2.86175	2.86175	4.4609	-17.40869 C_b	38	-17.40869 C_b	38	0.78155	0.78155	1	1	1	0.78155	-1.85836				102.41	102.8 (1,3-cyclopentadiene)
$\angle C_bC_cC_c$ $-H_2C_bHC_c=C_cHC_bH_2-$ cyclopentene	2.86175	2.53321	4.4272	-17.40869 C_b	38	-17.61330 C_b	42	0.78155	0.77247	1	1	1	0.77701	-1.85836				110.14	110.0 (cyclopentene)
$\angle C_aC_bC_c$ $-H_2C_aH_2C_bHC_c=C_cH-$ cyclopentene	2.91548	2.86175	4.5166	-17.20408 C_a	35	-17.40869 C_c	38	0.79085	0.78155	1	1	1	0.78620	-1.85836				102.85	103.0 (cyclopentene)
$\angle C_bC_aC_b$ $-C_bH_2C_aH_2C_bH_2-$ cyclopentene	2.91548	2.91548	4.5826	-17.20408 C_b	35	-17.20408 C_b	35	0.79085	0.79085	1	1	1	0.79085	-1.85836				103.61	104.0 (cyclopentene)

AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple H_2-type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule (C_6H_6) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

C_6H_6 can be considered a linear combination of three ethylene molecules wherein a $C-H$ bond of each CH_2 group of $H_2C=CH_2$ is replaced by a $C=C$ bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. The radius $r_{ethylene2sp^3}$ ($0.85252a_0$) of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ ($-15.95955\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E\left(C_{ethylene},2sp^3\right)$ ($-15.76868\ eV$) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.246). $E_T\left(C=C,2sp^3\right)$ ($-1.13380\ eV$) (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the $C=C$-bond MO is given by the difference between $E\left(C_{ethylene},2sp^3\right)$ and $E\left(C,2sp^3\right)$. C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the $2s$ and $2p$ shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each $2sp^3$ HO of each carbon atom initially has four unpaired electrons. Thus, the $6H$ atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3-hybridized carbon atoms contribute twenty-four electrons to form six $C-H$ bonds and six $C=C$ bonds. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. Each $C=C$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each $C-H$ and each $C=C$ bond comprises a linear combination

of one and two diatomic H_2-type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of $C=C$-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\begin{pmatrix} 3\left(2\ C2sp^3+0.75\ H_2\ MO\right)\rightarrow 3\left(\overset{4e}{C=C}\right)-ethylene-type-bond\ MO \\ \rightarrow 6\left(\overset{3e}{C=C}\right)-bond\ MO\ of\ benzene \end{pmatrix} \tag{15.142}$$

The linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond $C=C$-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the $C=C$-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each $C=C$-bond gives rise to the $C_{benzene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and C_2 of Eq. (15.42) for the aromatic $\overset{3e}{C=C}$-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=\frac{13.605804\ eV}{15.95955\ eV}=0.85252 \tag{15.143}$$

The energies of each $\overset{3e}{C=C}$ bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the $\overset{3e}{C=C}$ bonding of benzene wherein each of the six $\overset{3e}{C=C}$ bonds of benzene comprises $(0.75)(4)=3$ electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the $\overset{3e}{C=C}$ bonds of benzene, $E_T\left(C_6H_6,\overset{3e}{C=C}\right)$, is given by $(6)(0.75)$ times $E_{T+osc}(C=C)$ (Eq. (14.492)), the total energy of the $\overset{3e}{C=C}$-bond MO of benzene including the Doppler term, minus eighteen times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the $\overset{3e}{C=C}$ bonds of bond order two. Thus, the total energy of the six $\overset{3e}{C=C}$ bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned} E_T\left(C_6H_6,\overset{3e}{C=C}\right) &= (6)(0.75)E_{T+osc}(C=C)-(6)(3)E\left(C,2sp^3\right) \\ &= (6)(0.75)(-66.05796\ eV)-18(-14.63489\ eV) \\ &= -297.26081\ eV-(-263.42798\ eV) \\ &= -33.83284\ eV \end{aligned} \tag{15.144}$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds. $E_{h\nu}$ of an aromatic bond is given by $E_T\left(H_2\right)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_2-type MO such that

$$\overline{E}_{osc}=n_1\left(\overline{E}_D+\overline{E}_{Kvib}\right)=n_1\left(-31.63536831\ eV\sqrt{\frac{2\overline{E}_K}{Mc^2}}+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \tag{15.145}$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56). Multiplication of the total energy given by Eq. (15.55) by $f_1=0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_T(Group)=f_1\left(\begin{array}{l} E(basis\ energies)+E_T\left(atom-atom,msp^3.AO\right) \\ -31.63536831\ eV\sqrt{\dfrac{2\hbar\sqrt{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}{m_ec^2}}+n_1\overline{E}_{Kvib}+c_3\dfrac{8\pi\mu_o\mu_B^2}{r^3} \end{array}\right) \tag{15.146}$$

The total bond energy of the aromatic group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of $c_4 E_{initial}(c_4\ AO/HO)$ and $c_5 E_{initial}(c_5\ AO/HO)$:

$$E_D(Group) = -\left(f_1 \left(\begin{array}{l} E(basis\ energies) + E_T(atom-atom, msp^3.AO) \\ -31.63536831\ eV \sqrt{\dfrac{2\hbar\sqrt{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}} + n_1 \bar{E}_{Kvib} + c_3 \dfrac{8\pi\mu_o \mu_B^2}{r^3} \end{array} \right) - \left(c_4 E_{initial}(AO/HO) + c_5 E_{initial}(c_5\ AO/HO) \right) \right) \quad (15.147)$$

Since there are three electrons per aromatic bond, c_4 is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule (C_6H_6) section. The energy components of V_e, V_p, T, V_m, and E_T are the same as those of the hydrogen carbide radical, except that $E_T(C=C, 2sp^3) = -1.13379\ eV$ (Eq. (14.247)) is subtracted from $E_T(CH)$ of Eq. (13.495) to match the energy of each $C-H$-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T(atom-atom, msp^3.AO) = -1.13379\ eV$.

The total energy of the benzene $C-H$-bond MO, $E_{T_{benzene}}(C-H)$, given by Eq. (14.467) is the sum of $0.5E_T(C=C, 2sp^3)$, the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the formation of the corresponding $C\overset{3e}{=}C$-bond MO (Eq. (14.247)), and $E_{T_{benzene}}(CH)$, the σ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_1 = 1$ and $E_T(atom-atom, msp^3.AO) = \dfrac{-1.13379\ eV}{2}$. Thus, the energy

contribution to the single aromatic CH bond is one half that of the $C\overset{3e}{=}C$ double bond contribution. This matches the energies of the CH and $C\overset{3e}{=}C$ aromatic groups, conserves the electron number with the equivalent charge density as that of $s=1$ in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic $C\overset{3e}{=}C$ bonds to give CH groups creates unpaired electrons in these fragments that corresponds to $c_3=1$ in Eq. (15.56) with E_{mag} given by Eq. (15.58).

Each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each $C-H$ bond, $-E_{D_{benzene}}\left({}^{12}CH\right)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T\left(C_6H_6,C-H\right)$, given by Eq. (14.494) is

$$E_T\left(C_6H_6,C-H\right)=\left(6\right)\left(-E_{D_{benzene}}\left({}^{12}CH\right)\right)=6\left(-3.90454\ eV\right)=-23.42724\ eV \tag{15.148}$$

The total bond dissociation energy of benzene, $E_D\left(C_6H_6\right)$, given by Eq. (14.495) is the negative sum of $E_T\left(C_6H_6,C\overset{3e}{=}C\right)$ (Eq. (14.493)) and $E_T\left(C_6H_6,C-H\right)$ (Eq. (14.494)):

$$\begin{aligned}E_D\left(C_6H_6\right)&=-\left(E_T\left(C_6H_6,C\overset{3e}{=}C\right)+E_T\left(C_6H_6,C-H\right)\right)\\&=-\left(\left(-33.83284\ eV\right)+\left(-23.42724\ eV\right)\right)\\&=57.2601\ eV\end{aligned} \tag{15.149}$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each $E_D\left(Group\right)$ of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C}=C$
CH (aromatic)	CH (i)

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and experimental values [1].

Parameter	$\overset{3e}{C}=C$ Group	CH Group
$a\ (a_0)$	1.47348	1.60061
$c'\ (a_0)$	1.31468	1.03299
Bond Length $2c'\ (\AA)$	1.39140	1.09327
Exp. Bond Length $(\AA)$	1.399 (benzene)	1.101 (benzene)
$h,c\ (a_0)$	0.66540	1.22265
e	0.89223	0.64537

5 Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$\bar{E}(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C-H\ (CH)$	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\overset{3e}{C}=HC_{at}\overset{3e}{=}C$	C_{at}	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.216. The energy parameters (eV) of functional groups of aromatics and hertocyclics.

Parameters	$C=C^{3e}$ Group	CH Group
f_1	0.75	1
n_1	2	1
n_2	0	0
n_3	0	0
C_1	0.5	0.75
C_2	0.85252	1
c_1	1	1
c_2	0.85252	0.91771
c_3	0	1
c_4	3	1
c_5	0	1
C_{1o}	0.5	0.75
C_{2o}	0.85252	1
$V_e\ (eV)$	-101.12679	-37.10024
$V_p\ (eV)$	20.69825	13.17125
$T\ (eV)$	34.31559	11.58941
$V_m\ (eV)$	-17.15779	-5.79470
$E(AO/HO)\ (eV)$	0	-14.63489
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379
$E_T(AO/HO)\ (eV)$	0	-13.50110
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539
$E_T(atom-atom, msp^3.AO)\ (eV)$	-2.26759	-0.56690
$E_T(MO)\ (eV)$	-65.53833	-32.20226
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826
$E_K\ (eV)$	32.73133	17.43132
$\overline{E}_D\ (eV)$	-0.35806	-0.26130
$\overline{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)
$\overline{E}_{osc}\ (eV)$	-0.25982	-0.08364
$E_{mag}\ (eV)$	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Formula	Name	$C=C$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_6	Benzene	6	6	57.26008	57.26340	0.00006

Table 15.218. The bond angle parameters of benzene and experimental values [1]. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

NAPHTHALENE

Naphthalene has the formula $C_{10}H_8$ and comprises a planar molecule with two aromatic rings that share a common $C-C$ group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is $(0.75)(4)=3$ as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a $C-C$ single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging $C-C$ single bond, and 16 electrons form the eight $C-H$ single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond, c_4 is three times ten, the number of aromatic bonds. Similarly, the aromatic $C-H$ group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten $C2sp^3$ HOs bridged by the $C-C$ single bond, the parameters c_1, C_2, and C_{2o} of Eq. (15.42) are one for the $C-C$ group, C_{1o} and C_1 are 0.5, and c_2 given by Eq. (15.142) is $c_2\left(C2sp^3HO\right)=0.85252$. Otherwise, the solutions of the $C-C$ bond parameters are equivalent to those of the replaced $C-H$ groups with $E\left(AO/HO\right)=-14.63489\,eV$ and $\Delta E_{H_2MO}\left(AO/HO\right)=-1.13379\,eV$ in Eq. (15.41). Similarly, the energy parameters are determined using Eqs. (15.52-15.56) with $E_T\left(atom-atom,msp^3.AO\right)=\dfrac{-1.13379\,eV}{2}$.

The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 62. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.79-15.108) are given in Table 15.224.

Table 15.219. The symbols of functional groups of naphthalene.

Functional Group	Group Symbol
$C_u C_u$ (aromatic bond)	$C^{2r}=C$
CH (aromatic)	CH (i)
$C_b - C_h$ (bridging bond)	$C-C$

Table 15.220. The geometrical bond parameters of naphthalene and experimental values [1].

Parameter	$C^{2r}=C$ Group	CH Group	$C-C$ Group
$a\ (a_0)$	1.47348	1.60061	1.75607
$c'\ (a_0)$	1.31468	1.03299	1.32517
Bond Length $2c'\ (\text{Å})$	1.39140	1.09327	1.40250
Exp. Bond Length (Å)	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)
$h, c\ (a_0)$	0.66540	1.22265	1.15226
u	0.89223	0.64537	0.75462

Table 15.221. The MO to HO intercept geometrical bond parameters of naphthalene. E_T is $E_T(atom-atom, nsp^3, AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (CH)$	C	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C^{2r}=HC_u^{2r}=C$	C_u	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$C^{2r}=HC_h^{2r}=C$	C_h	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57038
$C^{2r}=C_u(C_u)^{2r}=C$	C_h	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	99.50	80.50	47.66	1.18269	0.14248
$(C_u)_2C_h-C_h(C_u)_2$	C_h	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903					

Table 15.222. The energy parameters (eV) of functional groups of naphthalene.

Parameters	$C=C$ Group	CH Group	$C-C$ Group
f_1	0.75	1	1
n_1	2	1	1
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	1
c_1	1	1	1
c_2	0.85252	0.91771	0.85252
c_3	0	1	0
c_4	3	1	2
c_5	0	1	0
C_{1o}	0.5	0.75	0.5
C_{2o}	0.85252	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-34.43791
$V_p\ (eV)$	20.69825	13.17125	10.26723
$T\ (eV)$	34.31559	11.58941	9.80539
$V_m\ (eV)$	-17.15779	-5.79470	-4.90270
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-1.13379
$E_T(AO/HO)\ (eV)$	0	-13.50110	-13.50110
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63529
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-0.56690
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.20226
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	23.6343
$E_K\ (eV)$	32.73133	17.43132	15.55648
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.25127
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.18971
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-32.39198
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0
$E_D(Group)\ (eV)$	5.63881	3.90454	3.12220

Table 15.223. The total bond energies of naphthalene calculated using the functional group composition and the energies of Table 15.222 compared to the experimental values [2].

Formula	Name	$C^{3e}=C$	CH	$C-C$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_{10}H_8$	Naphthalene	10	8	1	90.74658	90.79143	0.00049

Table 15.224. The bond angle parameters of naphthalene and experimental values [1]. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle C_a C_c C_c$ (naphthalene)	2.62936	2.65034	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				119.40	119.4 (naphthalene)
$\angle C_c C_a H$ (naphthalene)																119.40		120.30	
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

TOLUENE

Toluene has the formula C_7H_8 and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a CH_3 functional group and a $C-C$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The CH_3 functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a $C-C$ functional group that is are solved using the same principles as those used to solve the alkane functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons, $E(AO/HO)$ and $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.41) are $-15.35946\ eV$ (Eq. (14.155)) and $\frac{-1.13379\ eV}{2}$, respectively.

To meet the equipotential condition of the union of the aromatic and methyl $C2sp^3$ HOs of the $C-C$ single bond, the parameters c_1, C_2, and C_{2o} of Eq. (15.42) are one for the $C-C$ group, C_{1o} and C_1 are 0.5, and c_2 given by Eq. (13.430) is $c_2(C2sp^3HO)=0.91771$. To match the energies of the functional groups, $E_T(atom-atom,msp^3.AO)$ of the $C-C$-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is $-1.13379\ eV$ which is the same energy per $C2sp^3$ HO as that of the replaced $C-H$ group.

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.79-15.108) are given in Table 15.230.

Table 15.225. The symbols of functional groups of toluene.

Functional Group	Group Symbol
CC (aromatic bond)	$C^{2e}C$
CH (aromatic)	CH (i)
$C_v - C_k$ (CH_3 to aromatic bond)	$C - C$
CH_3 group	$C - H\ (CH_3)$

Table 15.226. The geometrical bond parameters of toluene and experimental values [1].

Parameter	$C^{2e}C$ Group	CH (i) Group	$C-C$ Group	$C-H\ (CH_3)$ Group
$a\ (a_0)$	1.47348	1.60061	2.06004	1.64920
$c'\ (a_0)$	1.31468	1.03299	1.43528	1.04856
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.51904	1.10974
Exp. Bond Length $(\AA)$	1.399 (toluene)	1.11 (avg.) (toluene)	1.524 (toluene)	1.11 (avg.) (toluene)
$h_i c\ (a_0)$	0.66540	1.22265	1.47774	1.27295
e	0.89223	0.64537	0.69673	0.63580

Table 15.227. The MO to HO intercept geometrical bond parameters of toluene. E_T is $E_T\left(atom-atom,\ msp^3\text{-}AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Overlap}\left(C2sp^3\right)$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_4 (a_0)
$C-H\ (C_vH_3)$	C_v	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	79.89	101.11	45.13	1.20367	0.15511
$C-H\ (C_kH)$	C_k	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C^{2e}=HC_r^{2e}=C$ $C^{2e}=(H_2C_v)C_k^{2e}=C$	C_r C_k	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(C^{3e}=\right)_2 C_k-C_vH_3$	C_v	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	73.38	106.62	34.97	1.68807	0.25279
$\left(C^{3e}=\right)_2 C_k-C_vH_3$	C_k	-0.56690	-0.85035	-0.85035	0	-153.88228	0.91771	0.79597	-17.09334	-16.90247	61.56	118.44	28.27	1.81430	0.37901

Table 15.228. The energy parameters (eV) of functional groups of toluene.

Parameters	$C=C$ Group	CH (i) Group	$C-C$ Group	CH_3 Group
f_1	0.75	1		
n_1	2	1	1	3
n_2	0	0	0	2
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	1
c_1	1	1	1	1
c_2	0.85252	0.91771	0.91771	0.91771
c_3	0	1	0	0
c_4	3	1	2	1
c_5	0	1	0	3
C_{1o}	0.5	0.75	0.5	0.75
C_{2o}	0.85252	1	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-29.95792	-107.32728
$V_p\ (eV)$	20.69825	13.17125	9.47952	38.92728
$T\ (eV)$	34.31559	11.58941	7.27120	32.53914
$V_m\ (eV)$	-17.15779	-5.79470	-3.63560	-16.26957
$E(AO/HO)\ (eV)$	0	-14.63489	-15.35946	-15.56407
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-0.56690	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	-14.79257	-15.56407
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63537	-67.69451
$E_T(atom-atom, msp^3.AO)\ (eV)$	-2.26759	-0.56690	-1.13379	0
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-32.76916	-67.69450
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826	16.2731	24.9286
$E_K\ (eV)$	32.73133	17.43132	10.71127	16.40846
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.21217	-0.25352
$\bar{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.14940 [53]	0.35532 (Eq. (13.458))
$\bar{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.13747	-0.22757
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-32.90663	-67.92207
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	-13.59844	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454	3.63685	12.49186

Table 15.229. The total bond energies of toluene calculated using the functional group composition and the energies of Table 15.228 compared to the experimental values [2].

Formula	Name	$C^{Ar}=C$	CH (i)	$C-C'$ Group	CH_3	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_7H_8	Toluene	6	5	1	1	69.48425	69.546	0.00088

Table 15.230. The bond angle parameters of toluene and experimental values [1]. E_T is $E_T\left(atom-atom_n,m,sp^3,AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{T,\text{Table 15.228}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{T,\text{Table 15.228}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

CHLOROBENZENES

Chlorobenzenes have the formula $C_6H_{6-m}Cl_m$ and comprise the benzene molecule with at least one hydrogen atom replaced by a chlorine atom corresponding to a $C-Cl$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to E_{osc}. Two types of $C-Cl$ functional groups can be identified based on symmetry that determine the parameter R in Eq. (15.48). One corresponds to the special case of 1,3,5 substitution and the other corresponds to other cases of single or multiple substitutions of Cl for H. P-dichlorobenzene is representative of the bonding with $R=a$. 1,2,3-trichlorbenzene is the particular case wherein is $R=b$. Also, beyond the binding of three chlorides E_{mag} is subtracted for each additional Cl due to the formation of an unpaired electrons on each $C-Cl$ bond.

The bond between the chlorine and aromatic ring comprises two $C-Cl$ functional groups that are solved using the same principles as those used to solve the alkyl chloride functional groups as given in the corresponding section wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and Cl AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. As in the case of alkyl chlorides, c_2 of Eq. (15.52) for each $C-Cl$-bond MO is one, and the energy matching condition is determined by the C_2 parameter given by Eq. (15.111) which is $C_2\left(C2sp^3HO\ to\ Cl\right)=0.81317$. To match energies within the MO that bridges the chlorine AO and aromatic carbon $C2sp^3$ HO, $E\left(AO/HO\right)$ and $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) are $-14.63489\,eV$ and $-2.99216\,eV$, respectively. The latter matches twice that of the replaced $C-H$-bond MO plus $E_T\left(atom-atom,msp^3.AO\right)$. To match the energies of the functional groups, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-Cl$-bond MO in Eq. (15.53) due to the charge donation from the C and Cl atoms to the MO is $-0.72457\,eV$ (Eq. (14.151)).

The symbols of the functional groups of chlorobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of chlorobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each chlorobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of chlorobenzenes determined using Eqs. (15.79-15.108) are given in Table 15.236.

Table 15.231. The symbols of functional groups of chlorobenzenes.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH (i)
$Cl-C$ (Cl to aromatic bond)	$C-Cl$ (a)
$Cl-C$ (Cl to aromatic bond of 1,3,5-trichlorbenzene)	$C-Cl$ (b)

Table 15.232. The geometrical bond parameters of chlorobenzenes and experimental values [1].

Parameter	$C^{3e}=C$ Group	$C'H$ (i) Group	$C'-Cl$ (a) Group	$C'-Cl$ (b) Group
$a\ (a_0)$	1.47348	1.60061	2.20799	2.20799
$c'\ (a_0)$	1.31468	1.03299	1.64782	1.64782
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.74397	1.74397
Exp. Bond Length $(\AA)$	1.400 (chlorobenzene)	1.083 (chlorobenzene)	1.737 (chlorobenzene)	1.737 (chlorobenzene)
$h,c\ (a_0)$	0.66540	1.22265	1.46967	1.46967
e	0.89223	0.64537	0.74630	0.74630

Table 15.233. The MO to HO intercept geometrical bond parameters of chlorobenzenes. E_T is $E_T(atom-atom,msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{C\text{-}Cbond}(C'2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C_hH)$	C'_h	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C'=HC'_h=C'$	C'_h	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(C'=\right)_2 C'_u-Cl$	C'_u	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	73.32	106.68	31.67	1.87911	0.23129
$\left(C'=\right)_2 C'_u-Cl$	Cl	-0.36229	0	0	0		1.05158	0.89582	15.18804		82.92	97.08	37.22	1.75824	0.11042
$C'_h=(Cl)C'_u=C'_h$ (C'_h bound to H or Cl)	C'_u	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45.35	59.47	0.74854	0.56614

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Table 13.23 A: The energy parameters (eV) of functional groups of chlorobenzenes.

Parameters	$C^{3e}=C$ Group	CH (i) Group	$C-Cl$ (a) Group	$C-Cl$ (b) Group
f_1	0.75	1		
n_1	2	1	1	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	0.81317	0.81317
c_1	1	1	1	1
c_2	0.85252	0.91771	1	1
c_3	0	1	0	0
c_4	3	1	2	2
c_5	0	1	0	0
C_{1o}	0.5	0.75	0.5	0.5
C_{2o}	0.85252	1	0.81317	0.81317
V_e (eV)	-101.12679	-37.10024	-31.85648	-31.85648
V_p (eV)	20.69825	13.17125	8.25686	8.25686
T (eV)	34.31559	11.58941	7.21391	7.21391
V_m (eV)	-17.15779	-5.79470	-3.60695	-3.60695
$E(_{AO/HO})$ (eV)	0	-14.63489	-14.63489	-14.63489
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-1.13379	-2.99216	-2.99216
$E_T(_{AO/HO})$ (eV)	0	-13.50110	-11.64273	-11.64273
$E_T(_{H_2MO})$ (eV)	-63.27075	-31.63539	-31.63539	-31.63539
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-0.72457	-0.72457
$E_T(_{MO})$ (eV)	-65.53833	-32.20226	-32.35994	-32.35994
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	8.03459	14.7956
E_K (eV)	32.73133	17.43132	5.28851	9.73870
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.14722	-0.19978
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.08059 [12]	0.08059 [12]
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.10693	-0.15949
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-49.54347	-32.28590	-32.46687	-32.51943
$E_{initial}(_{e_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(_{e_5\ AO/HO})$ (eV)	0	-13.59844	0	0
$E_D(_{Group})$ (eV)	5.63881	3.90454	3.19709	3.24965

Table 15.235. The total bond energies of chlorobenzenes calculated using the functional group composition and the energies of Table 15.234 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_{D(Group)}$ (eV) values based on composition is given by (15.58).

Formula	Name	$C^{3e}\equiv C$	CH (i)	$C-Cl$ (a) Group	$C-Cl$ (b) Group	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_5Cl	Chlorobenzene	6	5	1	0	0	56.55263	56.581	0.00051
$C_6H_4Cl_2$	m-dichlorobenzene	6	4	2	0	0	55.84518	55.852	0.00012
$C_6H_3Cl_3$	1,2,3-trichlorobenzene	6	3	3	0	0	55.13773	55.077	-0.00111
$C_6H_3Cl_3$	1,3,5-trichlorbenzene	6	3	0	1	0	55.29542	55.255	-0.00073
C_6Cl_6	Hexachlorobenzene	6	0	6	0	3	52.57130	52.477	-0.00179

Table 15.236. The bond angle parameters of chlorobenzenes and experimental values [1]. E_T is $E_T\left(atom-atom,nsp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Conjunctive}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_p $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	Cal. θ $(^\circ)$	Exp. θ $(^\circ)$
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 ($\angle CC(H)C$ chlorobenzene) 121.7 ($\angle CC(Cl)C$ chlorobenzene) 120 [50-52] (benzene)
$\angle CCH$ $\angle CCCl$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

PHENOL

Phenol has the formula C_6H_6O and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an OH functional group and a $C-O$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a $C-O$ functional group that is are solved using the same principles as those used to solve the alcohol functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and O AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the O AO has an energy of $E\left(O\right)=-13.61806\ eV$. To meet the equipotential condition of the union of the $C-O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the $C-O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2\left(arylC2sp^3HO\ to\ O\right) &= \frac{E(O)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right) \\ &= \frac{-13.61806\ eV}{-14.63489\ eV}(0.85252) \\ &= 0.79329 \end{aligned} \tag{15.150}$$

$E_{\eta}\left(atom-atom,msp^3.AO\right)$ of the $C-O$-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.49608\ eV$. It is based on the energy match between the OH group and the $C2sp^3$ HO of an aryl group and is given by the linear combination of $-0.92918\ eV$ (Eq. (14.513)) and $-1.13379\ eV$ (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of phenol are given in Tables 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.240

corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.79-15.108) are given in Table 15.242.

Table 15.237. The symbols of functional groups of phenol.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C}=C$
CH (aromatic)	CH (i)
Aryl C-O	$C-O$ (a)
OH group	OH

Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

Parameter	$\overset{3e}{C}=C$ Group	CH (i) Group	$C-O$ (a) Group	OH Group
$a\ (a_0)$	1.47348	1.60061	1.68220	1.26430
$c'\ (a_0)$	1.31468	1.03299	1.29700	0.91808
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.37268	0.971651
Exp. Bond Length $(\AA)$	1.397 avg. (phenol)	1.084 (phenol)	1.364 (phenol)	0.956 (phenol)
$b,c\ (a_0)$	0.66540	1.22265	1.07126	0.86925
e	0.89223	0.64537	0.77101	0.72615

Table 15.239. The MO to HO intercept geometrical bond parameters of phenol. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{C_aOH}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_hH)$	C_h	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\left(C_h\overset{3r}{=}\right)_2 C_aO-H$	O	-0.74804	0	0	0		1.00000	0.87363	-15.57379		115.79	64.21	64.82	0.53799	0.38009
$\left(C_h\overset{3r}{=}\right)_2 C_a-OH$	C_a	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$\left(C_h\overset{3r}{=}\right)_2 C_a-OH$	O	-0.74804	0	0	0		1.00000	0.87363	15.57379		106.51	73.49	51.43	1.04871	0.24829
$\left(C_h\overset{3r}{=}\right)_2 C_aOH$	C_a	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	133.88	46.12	58.55	0.76870	0.54598
$\left(\overset{3r}{=}(H)C_h\right)_2 C_aOH$	C_h	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.240. The energy parameters (eV) of functional groups of phenol.

Parameters	$C \overset{3e}{=} C$ Group	CH (i) Group	$C-O$ (a) Group	OH Group
f_1	0.75	1		
n_1	2	1	1	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	1
c_1	1	1	1	0.75
c_2	0.85252	0.91771	0.79329	1
c_3	0	1	0	1
c_4	3	1	2	1
c_5	0	1	0	1
C_{1o}	0.5	0.75	0.5	0.75
C_{2o}	0.85252	1	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-34.04658	-40.92709
$V_p\ (eV)$	20.69825	13.17125	10.49024	14.81988
$T\ (eV)$	34.31559	11.58941	10.11966	16.18567
$V_m\ (eV)$	-17.15779	-5.79470	-5.05983	-8.09284
$E(AO/HO)\ (eV)$	0	-14.63489	-14.63489	-13.6181
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	0	-1.13379	-1.49608	0
$E_T(AO/HO)\ (eV)$	0	-13.50110	-13.13881	-13.6181
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63539	-31.63532	-31.63247
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-1.49608	0
$E_T(MO)\ (eV)$	-65.53833	-32.20226	-33.13145	-31.63537
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	13.3984	44.1776
$E_K\ (eV)$	32.73133	17.43132	8.81907	29.07844
$\overline{E}_D\ (eV)$	-0.35806	-0.26130	-0.19465	-0.33749
$\overline{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.12808 [19]	0.46311 [17-18]
$\overline{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.13061	-0.10594
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.11441
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-33.26206	-31.74130
$E_{initial}(e_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-13.6181
$E_{initial}(e_5\ AO/HO)\ (eV)$	0	-13.59844	0	-13.59844
$E_D(Group)\ (eV)$	5.63881	3.90454	3.99228	4.41035

Table 15.241. The total bond energies of phenol calculated using the functional group composition and the energies of Table 15.240 compared to the experimental values [2].

Formula	Name	$C=C^{*}$	$(H(i)$	$(-()$ (a) Group	$(H$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy: (eV)	Relative Error
C_6H_6O	Phenol	6	5	1	1	61.75817	61.704	-0.000387

Table 15.242. The bond angle parameters of phenol and experimental values [1]. E_T is $E_T(atom-atom,hyp^{i},H(i))$.

Atoms in Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Tordwaller}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Tordwaller}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_0 (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.462956	2.462956	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85856				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle(C,OH$	2.59399	1.836616	3.6815	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				109.84	109.0 (phenol)

ANILNE

Aniline and methyl aniline have the formula C_6H_7N and C_7H_9N, respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an NH_2 functional group and a $C-N$ functional group. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The $C-C$ and CH_3 functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino (NH_2) functional group was solved using the procedure given in the Dihydrogen Nitride (NH_2) section. Using the results of Eqs. (13.245-13.368), the aryl amino parameters in Eq. (15.51) are $n_1=2$, $C_1=0.75$, $C_2=0.93613$ (Eqs. (13.248-13.249)), $C_{1o}=1.5$, and $c_1=0.75$. In the determination of the hybridization factor c_2 of Eq. (15.52) for the $N-H$-bond MO of aryl amines, the $C2sp^3$ HO of the $C-NH_2$-bond MO has an energy of $E\left(C,2sp^3\right)=-15.76868\ eV$ (Eq. (15.18) corresponding to $s=2$ in Eqs. (15.18-15.20), and the N AO has an energy of $E(N)=-14.53414\ eV$. To meet the equipotential condition of the union of the $N-H$ H_2-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 given by Eq. (15.68) is

$$c_2(H\ to\ \text{anline}\ N)=\frac{E(N)}{E\left(C,2sp^3\right)}=\frac{-14.53414\ eV}{-15.76868\ eV}=0.92171 \tag{15.151}$$

The bond between the amino and aromatic ring comprises a $C-N$ functional group that is the same as that of 2° amines (methylene) except that the energies corresponding to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the $2s$ and $2p$ AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and N AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The hybridization is determined in a similar manner to that of the $C-O$ group of phenol. In anilines, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (15.25)) and the N AO has an energy

of $E(N) = -14.53414\ eV$. To meet the equipotential condition of the union of the $C-O$ H_2-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.51) for the $C-O$-bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(arylC2sp^3HO\ to\ N) &= \frac{E(N)}{E(C,2sp^3)} c_2(arylC2sp^3HO) \\ &= \frac{-14.53414\ eV}{-14.63489\ eV}(0.85252) \\ &= 0.84665 \end{aligned} \tag{15.152}$$

$E_T(atom-atom, msp^3.AO)$ of the $C-N$-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379\ eV$ (Eq. (14.247)). It is based on the energy

match between the NH_2 group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl $C-H$ group that it replaces.

The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in Table 15.247 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.79-15.108) are given in Table 15.248.

Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

Functional Group	Group Symbol
CC (aromatic bond)	$C \overset{3e}{=} C$
CH (aromatic)	CH (i)
Aryl C-N	$C-N$ (a)
NH_2 group	NH_2
$C_a - C_h$ (CH_3 to aromatic bond)	$C-C$ (a)
CH_3 group	$C-H\ (CH_3)$

Table 15.244. The geometrical bond parameters of aniline and methyl-substituted anilines and experimental values [1].

Parameter	$C^{3\varepsilon}=C$ Group	CH (i) Group	$C-N$ (a) Group	NH_2 Group	$C-C$ (a) Group	$C-H\ (CH_3)$ Group
$a\ (a_0)$	1.47348	1.60061	1.81158	1.24428	2.06004	1.64920
$c'\ (a_0)$	1.31468	1.03299	1.34595	0.94134	1.43528	1.04856
Bond Length $2c'\ (\text{Å})$	1.39140	1.09327	1.42449	0.99627	1.51904	1.10974
Exp. Bond Length (Å)	1.397 avg. (phenol)	1.084 (phenol)	1.431 (aniline)	0.998 (aniline)	1.524 (toluene)	1.11 (avg.) (toluene)
$b,c\ (a_0)$	0.66540	1.22265	1.21254	0.81370	1.47774	1.27295
e	0.89223	0.64537	0.74297	0.75653	0.69673	0.63580

5 Table 15.245. The MO to HO intercept geometrical bond parameters of aniline and methyl-substituted anilines. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	$d_1\ (a_0)$	$d_2\ (a_0)$
$C-H\ (C_hH)$	C_h	-0.85035	-0.85035	-0.56690	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C-H\ (C_aH_3)$	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	79.89	101.11	43.13	1.20367	0.15511
$\left(C_h^{3\varepsilon}=\right)_2 C_aNH-H$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$\left(C_h^{3\varepsilon}=\right)_2 C_a-NH_2$	C_a	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	88.49	91.51	41.01	1.36696	0.02101
$\left(C_h^{3\varepsilon}=\right)_2 C_a-NH_2$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$\left(C^{3\varepsilon}=\right)_2 C_h-C_aH_3$	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	73.38	106.62	34.97	1.68807	0.25279
$\left(C^{3\varepsilon}=\right)_2 C_h-C_aH_3$	C_h	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90247	61.56	118.44	28.27	1.81430	0.37901
$C^{3\varepsilon}=HC_e^{3\varepsilon}=C'$ $C^{3\varepsilon}=\left(H_2N\right)C_a^{3\varepsilon}=C$ $C^{3\varepsilon}=\left(H_2C_a\right)C_h^{3\varepsilon}=C'$	C_e C_a C_h	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.246. The energy parameters (eV) of functional groups of aniline and methyl-substituted anilines.

Parameters	$C^{3e}=C$ Group	CH (i) Group	$C-N$ (a) Group	NH_2 Group	$C-C$ (a) Group	CH_3 Group
f_1	0.75	1				
n_1	2	1	1	2	1	3
n_2	0	0	0	0	0	2
n_3	0	0	0	1	0	0
C_1	0.5	0.75	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	0.93613	1	1
c_1	1	1	1	0.75	1	1
c_2	0.85252	0.91771	0.84665	0.92171	0.91771	0.91771
c_3	0	1	0	0	0	0
c_4	3	1	2	1	2	1
c_5	0	1	0	2	0	3
C_{1o}	0.5	0.75	0.5	1.5	0.5	0.75
C_{2o}	0.85252	1	1	1	1	1
V_e (eV)	-101.12679	-37.10024	-32.76465	-78.97795	-29.95792	-107.32728
V_p (eV)	20.69825	13.17125	10.10870	28.90735	9.47952	38.92728
T (eV)	34.31559	11.58941	9.04312	31.73641	7.27120	32.53914
V_m (eV)	-17.15779	-5.79470	-4.52156	-15.86820	-3.63560	-16.26957
$E(_{AO/HO})$ (eV)	0	-14.63489	-14.63489	-14.53414	-15.35946	-15.56407
$\Delta E_{H_2MO}(_{AO/HO})$ (eV)	0	-1.13379	-1.13379	0	-0.56690	0
$E_T(_{AO/HO})$ (eV)	0	-13.50110	-13.50110	-14.53414	-14.79257	-15.56407
$E(_{n_3\ AO/HO})$ (eV)	0	0	0	-14.53414	0	0
$E_T(_{H_2MO})$ (eV)	-63.27075	-31.63539	-31.63549	-48.73654	-31.63537	-67.69451
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-1.13379	0	-1.13379	0
$E_T(_{MO})$ (eV)	-65.53833	-32.20226	-32.76916	-48.73660	-32.76916	-67.69450
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	11.9890	68.9812	16.2731	24.9286
E_K (eV)	32.73133	17.43132	7.89138	45.40465	10.71127	16.40846
$\overline{E}_D$ (eV)	-0.35806	-0.26130	-0.18211	-0.42172	-0.21217	-0.25352
$\overline{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.40929 [22]	0.14940 [53]	0.35532 (Eq. (13.458))
$\overline{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.10462	-0.21708	-0.13747	-0.22757
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(_{Group})$ (eV)	-49.54347	-32.28590	-32.87379	-49.17075	-32.90663	-67.92207
$E_{initial}(_{e_4\ AO/HO})$ (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
$E_{initial}(_{e_5\ AO/HO})$ (eV)	0	-13.59844	0	-13.59844	0	-13.59844
$E_D(_{Group})$ (eV)	5.63881	3.90454	3.60401	7.43973	3.63685	12.49186

Table 15.247. The total bond energies of aniline and methyl-substituted anilines calculated using the functional group composition and the energies of Table 15.246 compared to the experimental values [2].

Formula	Name	$C^{Je}=C$	CH (i)	$C-N$ (a) Group	NH_2 Group	$C-C$ (a) Group	CH_3	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_6H_7N	Aniline	6	5	1	1	0	0	64.43373	64.374	-0.00093
C_7H_9N	2-methylaniline	6	4	1	1	1	1	76.62345	76.643	-0.00025
C_7H_9N	3-methylaniline	6	4	1	1	1	1	76.62345	76.661	0.00050
C_7H_9N	4-methylaniline	6	4	1	1	1	1	76.62345	76.654	0.00040

Table 15.248. The bond angle parameters of aniline and methyl-substituted anilines and experimental values [1]. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_p (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.93613 Eq. (13.248))	1	1	1	0.75	1.06823	0				113.89	113.9 (aniline)
$\angle HNC_a$	1.88268	2.69190	4.0332	-14.53414	N	-15.95955	9	0.84665 (Eq. (15.152))	0.86284 (Eq. (15.64))	0.75	1	0.75	1.01912	0				122.70	

ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an NO_2 functional group and a $C-N$ functional group. Examples include nitrobenzene, nitrophenol, and nitroanilne with formulas $C_6H_5NO_2$, $C_6H_5NO_3$, and $C_6H_6N_2O_2$, respectively. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH and $C-O$ functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The NH_2 and $C-N$ functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond energies of the nitroanilines given in Table 15.252 are due to differences in the E_{osc} term. For simplicity and since the differences are small, the E_{osc} terms for nitroanilines were taken as the same.

The NO_2 group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a $C-N$ functional group that is the same as that of nitroalkanes given in the corresponding section except that $E_T\left(atom-atom,msp^3.AO\right)$ is $-0.72457\,eV$, one half of that of the $C-N$-bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage , the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.79-15.108) are given in Table 15.254.

Table 15.249. The symbols of functional groups of aryl nitro compounds.

Functional Group	Group Symbol
CC (aromatic bond)	$C^{3e}C$
CH (aromatic)	CH (i)
Aryl C-N (aniline)	$C-N$ (a)
Aryl C-N (nitro)	$C-N$ (b)
Aryl C-O	$C-O$ (a)
NO_2 group	NO_2
NH_2 group	NH_2
OH group	OH

Table 15.250. The geometrical bond parameters of aryl nitro compounds and experimental values [1].

Parameter	$C^{3e}C$ Group	CH (i) Group	$C-N$ (a) Group	$C-N$ (b) Group	$C-O$ (a) Group	NO_2 Group	NH_2 Group	OH Group
$a\ (a_0)$	1.47348	1.60061	1.81158	1.97794	1.68220	1.33221	1.24428	1.26430
$c'\ (a_0)$	1.31468	1.03299	1.34595	1.40639	1.29700	1.15421	0.94134	0.91808
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.42449	1.48846	1.37268	1.22157	0.99627	0.971651
Exp. Bond Length $(\AA)$	1.397 avg. (phenol)	1.084 (phenol)	1.431 (aniline)		1.364 (phenol)	1.224 (nitromethane)	0.998 (aniline)	0.956 (phenol)
$b,c\ (a_0)$	0.66540	1.22265	1.21254	1.39079	1.07126	0.66526	0.81370	0.86925
e	0.89223	0.64537	0.74297	0.71104	0.77101	0.86639	0.75653	0.72615

Table 15.251. The MO to HO intercept geometrical bond parameters of aryl nitro compounds. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}\left(C2sp^3\right)$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_bH)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$\left(C_b^{3c}=\right)_2 C_aO-H$	O	-0.74804	0	0	0		1.00000	0.87363	-15.57379		115.79	64.21	64.82	0.53799	0.38009
$\left(C_b^{3c}=\right)_2 C_a-OH$	C_a	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
$\left(C_b^{3c}=\right)_2 C_a-OH$	O	-0.74804	0	0	0		1.00000	0.87363	15.57379		106.51	73.49	51.43	1.04871	0.24829
$\left(C_b^{3c}=\right)_2 C_aOH$	C_a	-0.74804	-0.85035	-0.85035	0	-154.06442	0.91771	0.78762	-17.27448	-17.08362	133.88	46.12	58.55	0.76870	0.54598
$C^{3c}=HC_c^{3c}=C$ $C^{3c}=\left(H_2N\right)C_a^{3c}=C$ $\left(^{3c}=\left(H\right)C_b\right)_2 C_aOH$ $C^{3c}=\left(H_2C_a\right)C_b^{3c}=C$	C_c C_a C_b C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(C_b^{3c}=\right)_2 C_aNH-H$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$\left(C_b^{3c}=\right)_2 C_a-NH_2$	C_a	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	88.49	91.51	41.01	1.36696	0.02101
$\left(C_b^{3c}=\right)_2 C_a-NH_2$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$\left(C^{3c}=\right)_2 C_b-C_aH_3$	C_a	-0.56690	0	0	0	-152.18259	0.91771	0.88392	-15.39265	-15.20178	73.38	106.62	34.97	1.68807	0.25279
$\left(C^{3c}=\right)_2 C_b-C_aH_3$	C_b	-0.56690	-0.85035	-0.85035	0	-153 88328	0.91771	0.79597	-17.09334	-16.90247	61.56	118.44	28.27	1.81430	0.37901
$RN(O)=O$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		135.25	44.75	66.05	0.54089	0.61333
$RN(O)=O$	N	-0.92918	-0.92918	-0.36229	0		0 93084	0.79816	-17.04640		132.36	47.64	62.44	0.61640	0.53781
$\left(C^{3c}=\right)_2 C_a-NO_2$	C_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	72.49	107.51	33.53	1.64875	0.24236
$\left(C^{3c}=\right)_2 C_a-NO_2$	N	-0.92918	-0.92918	-0.36229	0		0.93084	0.79816	-17.04640		71.53	108.47	32.98	1.65923	0.25284
$C^{3c}=\left(O_2N\right)C_a^{3c}=C$	C_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0 80561	-16.88873	-16.69786	134.65	45.35	59.47	0.74854	0.56614

Table 15.252. The energy parameters (eV) of functional groups of aryl nitro compounds.

Parameters	$C^{3e}=C$ Group	CH (i) Group	$C-N$ (a) Group	$C-N$ (b) Group	$C-O$ (a) Group	NO_2 Group	NH_2 Group	OH Group
f_1	0.75	1						
n_1	2	1	1	1	1	2	2	1
n_2	0	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	1	0
C_1	0.5	0.75	0.5	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	1	1	1	1	1	0.93613	1
c_1	1	1	1	1	1	1	0.75	0.75
c_2	0.85252	0.91771	0.84665	0.91140	0.79329	0.85987	0.92171	1
c_3	0	1	0	0	0	0	0	1
c_4	3	1	2	2	2	4	1	1
c_5	0	1	0	0	0	0	2	1
$C_{1\sigma}$	0.5	0.75	0.5	0.5	0.5	0.5	1.5	0.75
$C_{2\sigma}$	0.85252	1	1	1	1	1	1	1
V_e (eV)	-101.12679	-37.10024	-32.76465	-31.36351	-34.04658	-106.90919	-78.97795	-40.92709
V_p (eV)	20.69825	13.17125	10.10870	9.67426	10.49024	23.57588	28.90735	14.81988
T (eV)	34.31559	11.58941	9.04312	7.92833	10.11966	40.12475	31.73641	16.18567
V_m (eV)	-17.15779	-5.79470	-4.52156	-3.96416	-5.05983	-20.06238	-15.86820	-8.09284
$E(\text{локно})$ (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	0	-14.53414	-13.6181
$\Delta E_{H_2 MO}(\text{локно})$ (eV)	0	-1.13379	-1.13379	-0.72457	-1.49608	0	0	0
$E_T(\text{локно})$ (eV)	0	-13.50110	-13.50110	-13.91032	-13.13881	0	-14.53414	-13.6181
$E(n_2\ \text{локно})$ (eV)	0	0	0	0	0	0	-14.53414	0
$E_T(H_2 MO)$ (eV)	-63.27075	-31.63539	-31.63549	-31.63540	-31.63532	-63.27093	-48.73654	-31.63247
$E_T\left(atom-atom, msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-1.13379	-0.72457	-1.49608	-3.71673	0	0
$E_T(MO)$ (eV)	-65.53833	-32.20226	-32.76916	-32.35994	-33.13145	-66.98746	-48.73660	-31.63537
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	11.9890	17.8228	13.3984	19.0113	68.9812	44.1776
E_K (eV)	32.73133	17.43132	7.89138	11.73128	8.81907	12.51354	45.40465	29.07844
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.18211	-0.21927	-0.19465	-0.23440	-0.42172	-0.33749
$\bar{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.10539 [45]	0.12808 [19]	0.19342 [45]	0.40929 [22]	0.46311 [17-18]
$\bar{E}_{exc}$ (eV)	-0.25982	-0.08364	-0.10462	-0.16658	-0.13061	-0.13769	-0.21708	-0.10594
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441
$E_T(Group)$ (eV)	-49.54347	-32.28590	-32.87379	-32.52652	-33.26206	-67.26284	-49.17075	-31.74130
$E_{initial}(e_s\ \text{локно})$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-13.6181
$E_{initial}(e_s\ \text{локно})$ (eV)	0	-13.59844	0	0	0	0	-13.59844	-13.59844
$E_D(Group)$ (eV)	5.63881	3.90454	3.60401	3.25674	3.99228	8.72329	7.43973	4.41035

Table 15.253. The total bond energies of aryl nitro compounds calculated using the functional group composition and the energies of Table 15.252 compared to the experimental values [2]. The magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (e values based on composition is given by (15.58).

Formula	Name	$\overset{Je}{C=C}$	CH (i)	$C-N$ (a) Group	$C-N$ (b) Group	$C-O$ (a) Group	NO_2 Group	NH_2 Group	OH Group	E_{mag}	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_6H_5NO_2$	Nitrobenzene	6	5	0	1	0	1	0	0	1	65.18754	65.217	0.00046
$C_6H_4N_2O_5$	2,4-dinitrophenol	6	4	0	2	1	2	0	1	2	77.61308	77.642	0.00037
$C_6H_6N_2O_2$	2-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	6	4	1	1	0	1	1	0	0	72.47476	72.476	-0.00002

Table 15.254. The bond angle parameters of aryl nitro compounds and experimental values [1]. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle O_a NO_b$	2.30843	2.30843	4.1231	-16.68411 O_a	24	-16.68411 O_b	24	0.81549	0.81549	1	1	1	0.81549	-1.44915				126.52	123.2 [54] (nitrobenzene) 125.3 (nitromethane)
$\angle CNO$	2.81279	2.30843	4.4159	-17.45562	40	-13.61806	O	0.77945	0.85395 (Eq. (15.114))	1	1	1	0.81670	-1.65376				118.82	118.5 [54] (nitrobenzene)
$\angle C_a OH$	2.59399	1.83616	3.6515	-14.82575	I	-14.82575	I	1	0.91771	0.75	1	0.75	0.91771	0				109.84	109.0 (phenol)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.93613 Eq. (13.248))	1	1	1	0.75	1.06823	0				113.89	113.9 (aniline)
$\angle C_a NH$	2.69190	1.88268	3.9833	-15.95955	9	-14.53414	N	0.84665 (Eq. (15.152))	0.84665 (Eq. (15.152))	0.75	1	0.75	1.00000	0				120.05	

BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an $C-C(O)-OH$ moiety that comprises $C=O$ and OH functional groups that are the same as those of carboxylic acids given in the corresponding section. The single bond of aryl carbon to the carbonyl carbon atom, $C-C(O)$, is also a functional group. This group is also equivalent to the same group of carboxylic acids except that $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-1.29147\,eV$ which is a linear combination of $\frac{-1.13379\,eV}{2}$, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-H$ group that the $C-C(O)$ group replaces, and that of an independent $C2sp^3$ HO, $-0.72457\,eV$ (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas $C_7H_6O_2$, $C_7H_5O_2Cl$, and $C_7H_7NO_2$, respectively. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The NH_2 and $C-N$ functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The $C-Cl$ functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The $C-Cl$ functional group of 3 or 4-chlorobenzoic acids corresponding to ortho and para substitution is also equivalent to that of chlorobenzene, except that $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-0.92918\,eV$ (Eq. (14.513)) since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the $C2sp^3$ HO.

The symbols of the functional groups of benzoic acid compounds are given in Table 15.255. The corresponding designations of benzoic acid is shown in Figure 64. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of

each $E_D(Group)$ of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.79-15.108) are given in Table 15.260.

Table 15.255. The symbols of functional groups of benzoic acid compounds.

Functional Group	Group Symbol
CC (aromatic bond)	$C \overset{3e}{=} C$
CH (aromatic)	CH (i)
C-C(O)	$C-C(O)$
C=O (aryl carboxylic acid)	$C=O$
(O)C-O	$C-O$
OH group	OH
$Cl-C$ (Cl to aromatic bond of 2-chlorobenzoic acid)	$C-Cl$ (i)
$Cl-C$ (Cl to aromatic bond of 3 or 4-chlorobenzoic acid)	$C-Cl$ (ii)
Aryl C-N (aniline)	$C-N$
NH_2 group	NH_2

Table 15.256. The geometrical bond parameters of benzoic acid compounds and experimental values [1].

Parameter	$C=C$ Group	CH (i) Group	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	OH Group	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-N$ Group	NH_2 Group
$a\ (a_0)$	1.47348	1.60061	1.95111	1.29907	1.73490	1.26430	2.20799	2.19358	1.81158	1.24428
$c'\ (a_0)$	1.31468	1.03299	1.39682	1.13977	1.31716	0.91808	1.64782	1.64243	1.34595	0.94134
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.47833	1.20628	1.39402	0.971651	1.74397	1.73827	1.42449	0.99627
Exp. Bond Length $(\AA)$	1.399 (benzene)	1.101 (benzene)	1.48 [55] (benzoic acid)	1.214 (acetic acid)	1.393 (methyl formate)	0.972 (formic acid)	1.737 (chlorobenzene)	1.737 (chlorobenzene)	1.431 (aniline)	0.998 (aniline)
$b,c\ (a_0)$	0.66540	1.22265	1.36225	0.62331	1.12915	0.86925	1.46967	1.45403	1.21254	0.81370
e	0.89223	0.64537	0.71591	0.87737	0.75921	0.72615	0.74630	0.74874	0.74297	0.75653

Table 15.257. The MO to HO intercept geometrical bond parameters of benzoic acid compounds. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{C'valence}(C'2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C'_hH)$	C'_h	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C'=HC'_h=C'$ $C'=(HOOC'_a)C'_b=C'(H)_c$ $C'=(Cl)C'_a=C'_b(H)$ $C'=(H_2N)C'_a=C'_b(H)$	C'_h C'_c C'_b C'_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(C'_h=\right)_2 C'_a(O)O-H$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		115.09	64.91	64.12	0.55182	0.36625
$\left(C'_h=\right)_2 C'_a(O)-OH$	O	-0.92918	0	0	0		1.00000	0.86359	-15.75493		101.32	78.68	48.58	1.14765	0.16950
$\left(C'_h=\right)_2 C'_a(O)-OH$	C'_a	-0.92918	-1.34946	-0.64574	0	-154.54007	0.91771	0.76652	-17.75013	-17.55927	93.11	86.89	42.68	1.27551	0.04165
$\left(C'_h=\right)_2 C'_a(OH)=O$	O	-1.34946	0	0	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61784
$\left(C'_h=\right)_2 C'_a(OH)=O$	C'_a	-1.34946	-0.64574	-0.92918	0	-154.54007	0.91771	0.76652	-17.75013	-17.55927	134.03	45.97	62.14	0.60699	0.53278
$C'_c=(HOOC'_a)C'_b=C'_c$ (C'_b bound to H, Cl, or NH_2)	C'_b	-0.64574	-0.85035	-0.85035	0	-153.96212	0.91771	0.79232	-17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124
$\left(C'=\right)_2 C'_a-Cl$	Cl	-0.36229	0	0	0		1.05158	0.89582	15.18804		82.92	97.08	37.22	1.75824	0.11042
$\left(C'=\right)_2 C'_a-Cl$	C'_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	73.32	106.68	31.67	1.87911	0.23129
$C'_b=(Cl)C'_a=C'_b$ (C'_b bound to H or Cl)	C'_a	-0.36229	-0.85035	-0.85035	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	134.65	45.35	59.47	0.74854	0.56614
$\left(C'_h=\right)_2 C'_aNH-H$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$\left(C'_h=\right)_2 C'_a-NH_2$	C'_a	-0.56690	-0.85035	-0.85035	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	88.49	91.51	41.01	1.36696	0.02101
$\left(C'_h=\right)_2 C'_a-NH_2$	N	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$C'=(H_2N)C'_a=C'$	C'_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.258. The energy parameters (eV) of functional groups of benzoic acid compounds.

Parameters	$C=C$ Group	CH (i) Group	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	OH Group	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-N$ Group	NH_2 Group
J_1	0.75	1								
n_1	2	1	1	2	1	1	1	1	1	2
n_2	0	0	0	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0	0	0	1
C_1	0.5	0.75	0.5	0.5	0.5	0.75	0.5	0.5	0.5	0.75
C_2	0.85252	1	1	1	1	1	0.81317	0.81317	1	0.93613
c_1	1	1	1	1	1	0.75	1	1	1	0.75
c_2	0.85252	0.91771	0.91771	0.85395	0.85395	1	1	1	0.84665	0.92171
c_3	0	1	0	2	0	1	0	0	0	0
c_4	3	1	2	4	2	1	2	2	2	1
c_5	0	1	0	0	0	1	0	0	0	2
C_{1v}	0.5	0.75	0.5	0.5	0.5	0.75	0.5	0.5	0.5	1.5
C_{2v}	0.85252	1	1	1	1	1	0.81317	0.81317	1	1
V_e (eV)	-101.12679	-37.10024	-32.15216	-111.25473	-35.08488	-40.92709	-31.85648	-32.14474	-32.76465	-78.97795
V_p (eV)	20.69825	13.17125	9.74055	23.87467	10.32968	14.81988	8.25686	8.28394	10.10870	28.90735
T (eV)	34.31559	11.58941	8.23945	42.82081	10.11150	16.18567	7.21391	7.32700	9.04312	31.73641
V_{ee} (eV)	-17.15779	-5.79470	-4.11973	-21.41040	-5.05575	-8.09284	-3.60695	-3.66350	-4.52156	-15.86820
$E\{n_1,n_2,n_3\}$ (eV)	0	-14.63489	-14.63489	0	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.53414
$\Delta E_{n_1,n_2,n_3}(n_1,n_2,n_3)$ (eV)	0	-1.13379	-1.29147	-2.69893	-2.69893	0	-2.99216	-2.99216	-1.13379	0
$E_T(n_1,n_2,n_3)$ (eV)	0	-13.50110	-13.34342	2.69893	-11.93596	-13.6181	-11.64273	-11.64273	-13.50110	-14.53414
$E(n_1,n_2,n_3)$ (eV)	0	0	0	0	0	0	0	0	0	-14.53414
$E_T(n_1,n_2,n_3)$ (eV)	-63.27075	-31.63539	-31.63530	-63.27074	-31.63541	-31.63247	-31.63539	-31.63542	-31.63549	-48.73654
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-1.29147	-2.69893	-1.85836	0	-0.72457	-0.92918	-1.13379	0
$E_T(sm)$ (eV)	-65.53833	-32.20226	-32.92684	-65.96966	-33.49373	-31.63537	-32.35994	-32.56455	-32.76916	-48.73660
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	10.7262	59.4034	24.3637	44.1776	8.03459	8.11389	11.9890	68.9812
E_K (eV)	32.73133	17.43132	7.06019	39.10034	16.03660	29.07844	5.28851	5.34070	7.89138	45.40465
$\overline{E}_D$ (eV)	-0.35806	-0.26130	-0.17309	-0.40804	-0.26535	-0.33749	-0.14722	-0.14888	-0.18211	-0.42172
$\overline{E}_{Koh}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.10502 [29]	0.21077 [12]	0.14010 [31]	0.46311 [17-18]	0.08059 [12]	0.08059 [12]	0.15498 [54]	0.40929 [22]
$\overline{E}_{vac}$ (eV)	-0.25982	-0.08364	-0.12058	-0.30266	-0.19530	-0.10594	-0.10693	-0.10859	-0.10462	-0.21708
E_{surf} (eV)	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803
$E_T(Group)$ (eV)	-49.54347	-32.28590	-33.04742	-66.57498	-33.68903	-31.74130	-32.46687	-32.67314	-32.87379	-49.17075
$E_{mixed}(n_1,n_2,n_3)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.53414
$E_{mixed}(n_1,n_2,n_3)$ (eV)	0	-13.59844	0	0	0	-13.59844	0	0	0	-13.59844
$E_D(Group)$ (eV)	5.63881	3.90454	3.77764	7.80660	4.41925	4.41035	3.19709	3.40336	3.60401	7.43973

Table 15.259. The total bond energies of benzoic acid compounds calculated using the functional group composition and the energies of Table 15.258 compared to the experimental values [2].

Formula	Name	$C^{Je}=C$ Group	CH (i) Group	$C-C(O)$ Group	$C=O$ Group	$C-O$ Group	OH Group	$C-Cl$ (i) Group	$C-Cl$ (ii) Group	$C-N$ Group	NH_2 Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_7H_6O_2$	Benzoic acid	6	5	1	1	1	1	0	0	0	0	73.76938	73.762	-0.00009
$C_7H_5ClO_2$	2-chlorobenzoic acid	6	4	1	0	1	1	0	1	0	0	73.06193	73.082	0.00027
$C_7H_5ClO_2$	3-chlorobenzoic acid	6	4	1	1	1	1	0	1	0	0	73.26820	73.261	-0.00010
$C_7H_5ClO_2$	4-chlorobenzoic acid	6	4	1	1	1	1	0	1	0	0	73.26820	73.247	-0.00028
$C_7H_7NO_2$	Anilinc-2-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.941	0.00041
$C_7H_7NO_2$	Anilinc-3-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.813	-0.00118
$C_7H_7NO_2$	Anilinc-4-carboxylic acid	6	4	1	1	1	1	0	0	1	1	80.90857	80.949	0.00050

Table 15.260. The bond angle parameters of benzoic acid compounds and experimental values [1]. E_T is $E_T\left(atom-atom, nsp^3.AO\right)$.

Atoms of Angle	$2c^*$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Conjunction}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Conjunction}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_c (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle C_aO_bH$	2.63431	1.83616	3.6405	-14.82575	1	-14.82575	1	1	0.91771	0.75	1	0.75	0.91771	0				107.71	
$\angle C_bC_aO_a$	2.82796	2.27954	4.4721	-17.17218	34	-13.61806	O	0.79232	0.85395 (Eq. (15.114))	1	1	1	0.82313	-1.65376				121.86	122 [55] (benzoic acid)
$\angle C_bC_aO_a$	2.82796	2.63431	4.6690	-16.40067	19	-13.61806	O	0.82959	0.85395 (Eq. (15.114))	1	1	1	0.84177	-1.65376				117.43	118 [55] (benzoic acid)
$\angle O_aC_aO_b$	2.27954	2.63431	4.3818	-16.17521 O_a	12	-15.75493 O_b	7	0.84115	0.86359	1	1	1	0.85237	-1.44915				126.03	122 [55] (benzoic acid)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 ($\angle CC(H)C$ chlorobenzene) 121.7 ($\angle CC(Cl)C$ chlorobenzene) 120 [50-52] (benzene)
$\angle CCH$ $\angle CCCl$ (aromatic)																120.19		119.91	120 [50-52] (benzene)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.93615 Eq. (13.248))	1	1	1	0.75	1.06823	0				113.89	113.9 (aniline)
$\angle C_aNH$	2.69190	1.88268	3.9835	-15.95955	9	-14.53414	N	0.84665 (Eq. (15.152))	0.84665 (Eq. (15.152))	0.75	1	0.75	1.00000	0				120.05	

ANISOLE

Anisole has the formula C_7H_8O and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety $-O-CH_3$ to form an ether comprising aromatic and methyl functional groups as well as two types of $C-O$ functional groups, one for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic $\overset{3e}{C=C}$ and $C-H$ functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The CH_3 and methyl $C-O$ functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The $C-O$ functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether $C-O$ functional group except that $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-1.13379\,eV$ (Eq. (14.247)). $E_T\left(atom-atom,msp^3.AO\right)$ is based on the energy match between the OCH_3 group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl $C-H$ group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.79-15.108) are given in Table 15.266.

Table 15.261. The symbols of functional groups of anisole.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH (i)
Aryl C-O	$C-O$ (a)
Methyl C-O	$C-O$ (b)
CH_3 group	$C-H\left(CH_3\right)$

Table 15.262. The geometrical bond parameters of anisole and experimental values [1].

Parameter	$C^{3e}=C$ Group	$C'H$ (i) Group	$C'-O$ (a) Group	$C-O$ (b) Group	$C'-H\ (CH_3)$ Group
$a\ (a_0)$	1.47348	1.60061	1.82682	1.80717	1.64920
$c'\ (a_0)$	1.31468	1.03299	1.35160	1.34431	1.04856
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.43047	1.42276	1.10974
Exp. Bond Length $(\AA)$	1.397 avg. (phenol)	1.084 (phenol)			1.11 (avg.) (toluene)
$b,c\ (a_0)$	0.66540	1.22265	1.22900	1.20776	1.27295
e	0.89223	0.64537	0.73986	0.74388	0.63580

Table 15.263. The MO to HO intercept geometrical bond parameters of anisole. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C'2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C'2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C_hH)$	C'_h	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C'-H\ (OC'_eH_3)$	C'_e	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	78.85	101.15	42.40	1.21777	0.16921
$\left(C_h^{3e}=\right)_2 C_aO-C_eH_3$	C'_e	-0.72457	0	0	0	-152.34026	0.91771	0.87495	-15.55033	-15.35946	95.98	84.02	46.10	1.25319	0.09112
$\left(C_h^{3e}=\right)_2 C_aO-C_eH_3$	O	-0.72457	-0.56690	0	0		1.00000	0.84418	-16.11722		93.38	86.62	44.25	1.29456	0.04975
$\left(C_h^{3e}=\right)_2 C_a-OC_eH_3$	C'_a	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	87.00	93.00	40.30	1.39329	0.04170
$\left(C_h^{3e}=\right)_2 C_a-OC_eH_3$	O	-0.56690	-0.72457	0	0		1.00000	0.84418	-16.11722		91.59	88.41	43.36	1.32814	0.02346
$\left(C_h^{3e}=\right)_2 C'_aOC'_eH_3$	C'_a	-0.56690	-0.85035	-0.85035	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$\left(^{3e}=(H)C'_h\right)_2 C'_aOC'_eH_3$	C'_h	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.264. The energy parameters (eV) of functional groups of anisole.

Parameters	$C^{3e}=C$ Group	CH (i) Group	$C-O$ (a) Group	$C-O$ (b) Group	CH_3 Group
f_1	0.75	1			
n_1	2	1	1	1	3
n_2	0	0	0	0	2
n_3	0	0	0	0	0
C_1	0.5	0.75	0.5	0.5	0.75
C_2	0.85252	1	1	1	1
c_1	1	1	1	1	1
c_2	0.85252	0.91771	0.85395	0.85395	0.91771
c_3	0	1	0	0	0
c_4	3	1	2	2	1
c_5	0	1	0	0	3
C_{1o}	0.5	0.75	0.5	0.5	0.75
C_{2o}	0.85252	1	1	1	1
$V_e\ (eV)$	-101.12679	-37.10024	-32.67197	-33.15757	-107.32728
$V_p\ (eV)$	20.69825	13.17125	10.06645	10.12103	38.92728
$T\ (eV)$	34.31559	11.58941	8.94231	9.17389	32.53914
$V_m\ (eV)$	-17.15779	-5.79470	-4.47115	-4.58695	-16.26957
$E_{\{AOMO\}}\ (eV)$	0	-14.63489	-14.63489	-14.63489	-15.56407
$\Delta E_{\Pi_2 MO\{AOMO\}}\ (eV)$	0	-1.13379	-1.13379	-1.44915	0
$E_{T\{AOMO\}}\ (eV)$	0	-13.50110	-13.50110	-13.18574	-15.56407
$E_{T\{\Pi_2 MO\}}\ (eV)$	-63.27075	-31.63539	-31.63547	-31.63533	-67.69451
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-1.13379	-1.44915	0
$E_{T\{MO\}}\ (eV)$	-65.53833	-32.20226	-32.76916	-33.08452	-67.69450
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	11.8393	12.0329	24.9286
$E_K\ (eV)$	32.73133	17.43132	7.79284	7.92028	16.40846
$\overline{E}_D\ (eV)$	-0.35806	-0.26130	-0.18097	-0.18420	-0.25352
$\overline{E}_{Kvib}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.13663 [21]	0.13663 [21]	0.35532 (Eq. (13.458))
$\overline{E}_{osc}\ (eV)$	-0.25982	-0.08364	-0.11266	-0.11589	-0.22757
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{T\{Group\}}\ (eV)$	-49.54347	-32.28590	-32.88182	-33.20040	-67.92207
$E_{initial\{c_4 .AOMO\}}\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial\{c_5 .AOMO\}}\ (eV)$	0	-13.59844	0	0	-13.59844
$E_{D\{Group\}}\ (eV)$	5.63881	3.90454	3.61204	3.93062	12.49186

Table 15.265. The total bond energies of anisole calculated using the functional group composition and the energies of Table 15.264 compared to the experimental values [2].

Formula	Name	$C^{Ar}=C$	CH (i)	$C-O$ (a) Group	$C-O$ (b) Group	CH_3 Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_7H_8O	Anisole	6	5	1	1	1	73.39006	73.355	-0.00047

Table 15.266. The bond angle parameters of anisole and experimental values [1]. E_T is $E_T\left(atom-atom, nsp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.A)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	34	-17.17218	34	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

PYRROLE

Pyrrole having the formula C_4H_5N comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to a NH functional group. The two symmetrical carbon-to-nitrogen bonds comprise the $C-N-C$ functional group. The 1,3-butdiene moiety comprises $C-C$, $C=C$, and CH functional groups. The $C-C$ and $C=C$ groups are equivalent to the corresponding groups of 1,3-butdiene given in the Cyclic and Conjugated Alkenes section except that the energies terms of the corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-butdiene except that the hybridization terms c_2 of the $C-C$ and $C=C$ groups and C_2 and C_{2o} of the $C=C$ group in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $(C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=0.85252)$, in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond character in the carbon-heteroatom bonding.

The NH group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term c_2 is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the CH functional group is equivalent to that of 1,3-butdiene, except that $\Delta E_{H_2MO}\left(AO/HO\right)=-2.26758\,eV$ (Eq. (14.247)) in Eq. (15.42) in order to provide matching double-bond character.

The solution of the $C-N-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.152)) matches the double-bond character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52)

become that of benzene given by Eq. (15.143), $C_2\left(benzeneC2sp^3HO\right)=0.85252$. Furthermore, $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-0.92918\,eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\,eV$ in total. This is the maximum energy for a single bond and corresponds to methylene character as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 65. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.79-15.108) are given in Table 15.272.

Table 15.267. The symbols of functional groups of pyrrole.

Functional Group	Group Symbol
$C_a=C_b$ double bond	$C=C$
C_b-C_h	$C-C$
C_a-N-C_a	$C-N-C$
NH group	NH
CH	CH

Table 15.268. The geometrical bond parameters of pyrrole and experimental values [1].

Parameter	$C=C$ Group	$C-C$ Group	$C-N-C$ Group	NH Group	CH Group
$a\ (a_0)$	1.45103	1.77965	1.43222	1.24428	1.53380
$c'\ (a_0)$	1.30463	1.33404	1.29614	0.94134	1.01120
Bond Length $2c'\ (\text{Å})$	1.38076	1.41188	1.37178	0.996270	1.07021
Exp. Bond Length (Å)	1.382 (pyrrole)	1.417 (pyrrole)	1.370 (pyrrole)	0.996 (pyrrole)	1.076 (pyrrole)
$b,c\ (a_0)$	0.63517	1.17792	0.60931	0.81370	1.15326
e	0.89910	0.74961	0.90499	0.75653	0.65928

Table 15.269. The MO to HO intercept geometrical bond parameters of pyrrole. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^2.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C'2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C'_aH)$	C'_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C'-H\ (C'_bH)$	C'_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C'_a=(H)C'_b-C'_b(H)=C'_a$	C'_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C'_a=C'_b(H)(H)C'_b=C'_a$	C'_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$HNC'_a=C'_b(H)$	C'_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C'_a(H)N-C'_a=C'_b(H)$	C'_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	138.54	41.46	61.09	0.69238	0.60376
$C'_a(H)N-C'_a=C'_a(H)$	N	-0.92918	-0.92918	0	0		0.93084	0.81549	-16.68411		138.92	41.08	61.59	0.68147	0.61467
$N-H\ (NH)$	N	-0.92918	-0.92918	0	0		0.93084	0.81549	-16.68411		117.34	62.66	62.90	0.56678	0.37456

Table 15.270. The energy parameters (eV) of functional groups of pyrrole.

Parameters	$C=C$ Group	$C-C$ Group	$C-N-C$ Group	NH Group	CH Group
n_1	2	1	2	1	1
n_2	0	0	0	0	0
n_3	0	0	0	0	0
C_1	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	1	0.85252	0.93613	1
c_1	1	1	1	0.75	1
c_2	0.85252	0.85252	0.84665	0.92171	0.91771
c_3	0	0	0	1	1
c_4	4	2	4	1	1
c_5	0	0	0	1	1
$C_{1\upsilon}$	0.5	0.5	0.5	0.75	0.75
$C_{2\upsilon}$	0.85252	1	0.85252	1	1
$V_e\ (eV)$	-104.37986	-33.80733	-106.58684	-39.48897	-39.09538
$V_p\ (eV)$	20.85777	10.19898	20.99432	14.45367	13.45505
$T\ (eV)$	35.96751	9.49831	37.21047	15.86820	12.74462
$V_m\ (eV)$	-17.98376	-4.74915	-18.60523	-7.93410	-6.37231
$E_{(AO/HO)}\ (eV)$	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_2MO\,(AO/HO)}\ (eV)$	-2.26759	-1.85836	-3.71673	0	-2.26758
$E_{T\,(AO/HO)}\ (eV)$	2.26759	-12.77653	3.71673	-14.53414	-12.36731
$E_{T\,(H_2MO)}\ (eV)$	-63.27075	-31.63572	-63.27056	-31.63534	-31.63533
$E_{T}\left(atom-atom, msp^3.AO\right)\ (eV)$	-2.26759	-2.26759	-3.71673	0	0
$E_{T\,(MO)}\ (eV)$	-65.53833	-33.90295	-66.98746	-31.63537	-31.63537
$\omega\ \left(10^{15}\ rad/s\right)$	15.4421	12.3131	15.7474	48.7771	28.9084
$E_K\ (eV)$	10.16428	8.10471	10.36521	32.10594	19.02803
$\overline{E}_D\ (eV)$	-0.20668	-0.19095	-0.21333	-0.35462	-0.27301
$\overline{E}_{Kvib}\ (eV)$	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.40696 [24]	0.39427 [56]
$\overline{E}_{osc}\ (eV)$	-0.11720	-0.11680	-0.15754	-0.15115	-0.07587
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{T\,(Group)}\ (eV)$	-65.77272	-34.01976	-67.30254	-31.78651	-31.71124
$E_{initial\,(c_4\ AO/HO)}\ (eV)$	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{initial\,(c_5\ AO/HO)}\ (eV)$	0	0	0	-13.59844	-13.59844
$E_{D\,(Group)}\ (eV)$	7.23317	4.74998	8.76298	3.51208	3.32988

Table 15.271. The total bond energies of pyrrole calculated using the functional group composition and the energies of Table 15.270 compared to the experimental values [2].

Formula	Name	$C=C$	$C'-C'$	$C'-N-C'$	NH	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_5N	Pyrrole	2	1	1	1	4	44.81090	44.785	-0.00057

Table 15.272. The bond angle parameters of pyrrole and experimental values [1]. In the calculation of θ_e, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{C'valence}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.B)	$E_{C'valence}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC'_aN$	2.02241	2.59228	4.0166	-14.82575	1	-14.53414	N	0.91771	0.92171 Eq. (15.151))	0.75	1	0.75	1.00435	0				120.51	121.5 (pyrrole)
$\angle C'_bC'_aH_e$																120.51	107.52	131.97	
$\angle HNC'_a$	1.88268	2.59228	3.8987	-14.53414	N	-16.49325	6	0.84665 (Eq. (15.152))	0.82493 (Eq. (15.64))	0.75	1	0.75	0.97435	0				120.37	
$\angle H_bC'_bC'_b$	2.02241	2.66807	4.2111	-16.88873 C'_b	15	-15.95954 C'_b	6	0.80561	0.85252	0.75	1	0.75	1.05822	0				127.20	127.1 (pyrrole)
$\angle H_aC'_aC'_b$	2.02241	2.60925	4.2111	-16.88873 C'_a	15	-15.95954 C'_b	6	0.80561	0.85252	0.75	1	0.75	1.05822	0				130.36	
$\angle H_bC'_bC'_a$	2.02241	2.60925	4.1312	-17.09334 C'_b	18	-16.47951 C'_a	11	0.79597	0.82562	0.75	1	0.75	1.03725	0				125.76	
$\angle C'_bC'_bH_b$																125.76	107.01	127.23	127.1 (pyrrole)
$\angle NC'_aC'_b$	2.59228	2.60925	4.1952	-14.53414	N	-17.09334 C'_b	18	0.84665 (Eq. (15.152))	0.79597	1	1	1	0.82131	-1.44915				107.52	107.7 (pyrrole)
$\angle C'_aNC'_a$	2.59228	2.59228	4.2426	-17.81791	26	-17.81791	26	0.76360	0.76360	1	1	1	0.76360	-1.85836				109.83	109.8 (pyrrole)
$\angle C'_aC'_bC'_b$	2.60925	2.66807	4.2426	-17.81791	26	-18.02252	29	0.76360	0.75493	1	1	1	0.75927	-1.85836				107.01	107.4 (pyrrole)

FURAN

Furan having the formula C_4H_4O comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the $C-O-C$ functional group. The 1,3-butdiene moiety comprises $C-C$, $C=C$, and CH functional groups. The CH, $C-C$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The $C-O-C$ functional group of furan is solved in a similar manner as that of the $C-N-C$ group of pyrrole. The solution of the $C-O-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-O-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ O\right)=0.79329$ (Eq. (15.150)) matches the double-bond character of the $C2sp^3$ HOs to the O atom, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2\left(benzeneC2sp^3HO\right)=0.85252$. Furthermore, $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) is $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of furan are given in Table 15.273. The structure of furan is shown in Figure 66. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.276 corresponding to functional-group composition of the molecule. The bond angle parameters of furan determined using Eqs. (15.79-15.108) are given in Table 15.278.

Table 15.273. The symbols of functional groups of furan.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C=C$
$C_b - C_b$	$C-C$
$C_a - O - C_a$	$C-O-C$
CH	CH

Table 15.274. The geometrical bond parameters of furan and experimental values [1].

Parameter	$C=C$ Group	$C-C$ Group	$C-O-C$ Group	CH Group
$a\ (a_0)$	1.45103	1.77965	1.41546	1.53380
$c'\ (a_0)$	1.30463	1.33404	1.28854	1.01120
Bond Length $2c'\ (A)$	1.38076	1.41188	1.36373	1.07021
Exp. Bond Length (A)	1.361 (furan)	1.431 (furan)	1.362 (furan)	1.075 (furan)
$b,c\ (a_0)$	0.63517	1.17792	0.58583	1.15326
e	0.89910	0.74961	0.91033	0.65928

Table 15.275. The MO to HO intercept geometrical bond parameters of furan. R_1 is an alkyl group and R, R', R'' are H or alkyl groups. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	r_{mitad} (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_a H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C-H\ (C_b H)$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_a = (H)C_b - C_b(H) = C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_a = C_b(H)(H)C_b = C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$OC_a = C_b(H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C_a O - C_a = C_b(H)$	C_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	140.16	39.84	61.75	0.66992	0.61862
$C_a O - C_a = C_b(H)$	O	-0.92918	-0.92918	0	0		1.00000	0.81549	-16.68411		140.52	39.48	62.25	0.65906	0.62947

Table 15.276. The energy parameters (eV) of functional groups of furan.

Parameters	$C=C$ Group	$C-C$ Group	$C-O-C$ Group	CH Group
n_1	2	1	2	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.5	0.5	0.75
C_2	0.85252	1	0.85252	1
c_1	1	1	1	1
c_2	0.85252	0.85252	0.79329	0.91771
c_3	0	0	0	1
c_4	4	2	4	1
c_5	0	0	0	1
C_{1o}	0.5	0.5	0.5	0.75
C_{2o}	0.85252	1	0.85252	1
$V_e\ (eV)$	-104.37986	-33.80733	-102.49036	-39.09538
$V_p\ (eV)$	20.85777	10.19898	21.11822	13.45505
$T\ (eV)$	35.96751	9.49831	36.20391	12.74462
$V_m\ (eV)$	-17.98376	-4.74915	-18.10196	-6.37231
$E(AO/HO)\ (eV)$	0	-14.63489	0	-14.63489
$\Delta E_{H_2MO}(AO/HO)\ (eV)$	-2.26759	-1.85836	0	-2.26758
$E_T(AO/HO)\ (eV)$	2.26759	-12.77653	0	-12.36731
$E_T(H_2MO)\ (eV)$	-63.27075	-31.63572	-63.27019	-31.63533
$E_T\left(atom-atom, msp^3.AO\right)\ (eV)$	-2.26759	-2.26759	-3.71673	0
$E_T(MO)\ (eV)$	-65.53833	-33.90295	-66.98746	-31.63537
$\omega\ \left(10^{15}\ rad/s\right)$	15.4421	12.3131	58.0664	28.9084
$E_K\ (eV)$	10.16428	8.10471	38.22034	19.02803
$\overline{E}_D\ (eV)$	-0.20668	-0.19095	-0.40965	-0.27301
$\overline{E}_{Kvib}\ (eV)$	0.17897 [6]	0.14829 [48]	0.12523 [57]	0.39427 [56]
$\overline{E}_{osc}\ (eV)$	-0.11720	-0.11680	-0.34704	-0.07587
$E_{mag}\ (eV)$	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-65.77272	-34.01976	-67.68154	-31.71124
$E_{initial}(c_4\ AO/HO)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c_5\ AO/HO)\ (eV)$	0	0	0	-13.59844
$E_D(Group)\ (eV)$	7.23317	4.74998	9.14198	3.32988

Table 15.277. The total bond energies of furan calculated using the functional group composition and the energies of Table 15.276 compared to the experimental values [2].

Formula	Name	$C=C$	$C-C$	$C-O-C$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C4H4O	Furan	2	1	1	4	41.67782	41.692	0.00033

Table 15.278. The bond angle parameters of furan and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aO$	2.02241	2.57707	3.9328	-16.88873	15	-13.61806	O	0.80561	0.79329 Eq. (15.150))	0.75	1	0.75	0.98470	0				117.02	115.9 (furan)
$\angle C_bC_aH_a$																117.02	110.69	132.29	
$\angle H_bC_bC_b$	2.02241	2.66807	4.2269	-16.88873 C_b	15	-15.95954 C_b	6	0.80561	0.85252	0.75	1	0.75	1.05822	0				128.09	128.0 (furan)
$\angle H_aC_aC_b$	2.02241	2.60925	4.2269	-16.88873 C_a	15	-15.95954 C_b	6	0.80561	0.85252	0.75	1	0.75	1.05822	0				131.32	
$\angle H_bC_bC_a$	2.02241	2.60925	4.1312	-17.09334 C_b	18	-16.47951 C_a	11	0.79597	0.82562	0.75	1	0.75	1.03725	0				125.76	
$\angle C_bC_bH_b$																125.76	107.01	127.23	128.0 (furan)
$\angle C_bC_aO$	2.60925	2.57707	4.2661	-17.09334 C_b	18	-13.61806	O	0.79597	0.79329 Eq. (15.150))	1	1	1	0.79463	-1.65376				110.69	110.7 (furan)
$\angle C_aOC_a$	2.57707	2.57707	4.1231	-18.22713	30	-18.22713	30	0.74646	0.74646	1	1	1	0.74646	-1.85836				106.25	106.6 (furan)
$\angle C_aC_bC_b$	2.60925	2.66807	4.2426	-17.81791	26	-18.02252	29	0.76360	0.75493	1	1	1	0.75927	-1.85836				107.01	106.1 (furan)

THIOPHENE

Thiophene having the formula C_4H_4S comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the $C-S-C$ functional group. The 1,3-butdiene moiety comprises $C-C$, $C=C$, and CH functional groups. The CH, $C-C$, and $C=C$ groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The $C-S-C$ functional group of thiophene is solved in a similar manner as that of the $C-N-C$ group of pyrrole and the $C-O-C$ group of furan. The solution of the $C-S-C$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the $C-S-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.42) and (15.52).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is $c_2\left(benzeneC2sp^3HO\right)=0.85252$ to match the double-bond character of the $C2sp^3$ HOs, and the energy matching condition is further determined by the C_2 parameter. Using the energy of S, $E\left(S\right)=-10.36001\,eV$ in Eq. (15.68) and the $C2sp^3$ HO energy of $E\left(C,2sp^3\right)=-15.76868\,eV$ (Eq. (15.18) corresponding to $s=2$ in Eqs. (15.18-15.20), the hybridization factor C_2 of Eq. (15.52) for the $C-S-C$-bond MO is

$$C_2\left(S3p\ to\ \text{aryl-type}\ C2sp^3HO\right)=\frac{E(S,3p)}{E\left(C,2sp^3\right)}=\frac{-10.36001\,eV}{-15.76868\,eV}=0.65700 \qquad (15.153)$$

C_{1o} is also given by Eq. (15.153). Furthermore, $\Delta E_{H_2MO}\left(AO/HO\right)$ of the $C-S-C$-bond MO in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-0.72457\,eV$ per atom corresponding to $-2.89830\,eV$ in total. The energy contribution equivalent to that of a methyl group (Eq. (14.151)) and that of the $C-S$-bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the $C2sp^3$ HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 67. The geometrical (Eqs. (15.1-15.5) and (15.42)),

intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.282 corresponding to functional-group composition of the molecule. The bond angle parameters of thiophene determined using Eqs. (15.79-15.108) are given in Table 15.284.

Table 15.279. The symbols of functional groups of thiophene.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C=C$
$C_b - C_b$	$C-C$
$C_a - S - C_a$	$C-S-C$
CH	CH

Table 15.280. The geometrical bond parameters of thiophene and experimental values [1].

Parameter	$C=C$ Group	$C-C$ Group	$C-S-C$ Group	CH Group
$a\ (a_0)$	1.45103	1.77965	1.74058	1.53380
$c'\ (a_0)$	1.30463	1.33404	1.62766	1.01120
Bond Length $2c'\ (\AA)$	1.38076	1.41188	1.72264	1.07021
Exp. Bond Length $(\AA)$	1.370 (thiophene)	1.423 (thiophene)	1.714 (thiophene)	1.078 (thiophene)
$h,c\ (a_0)$	0.63517	1.17792	0.61671	1.15326
e	0.89910	0.74961	0.93513	0.65928

Table 15.281. The MO to HO intercept geometrical bond parameters of thiophene. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,m\text{-}sp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	84.49	95.51	44.74	1.08953	0.07833
$C-H\ (C_bH)$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	82.21	97.79	43.14	1.11914	0.10794
$C_a=(H)C_b-C_b(H)=C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	91.57	88.43	42.49	1.31226	0.02177
$C_a=C_b(H)(H)C_b=C_a$	C_b	-1.13380	-1.13380	0	0	-153.88328	0.91771	0.79597	-17.09334	-16.90248	136.36	43.64	59.86	0.72857	0.57606
$SC_a=C_b(H)$	C_a	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	137.14	42.86	60.85	0.70685	0.59777
$C_aS-C_a=C_b(H)$	C_a	-1.13380	-0.72457	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49326	141.52	38.48	55.36	0.98926	0.63840
$C_aS-C_a=C_b(H)$	S	-0.72457	-0.72457	0	0		1.3201	0.83600	-16.27490		142.17	37.83	56.24	0.96733	0.66033

Table 15.282. The energy parameters (eV) of functional groups of thiophene.

Parameters	$C=C$ Group	$C-C$ Group	$C-S-C$ Group	CH Group
n_1	2	1	2	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.5	0.5	0.75
C_2	0.85252	1	0.65700	1
c_1	1	1	1	1
c_2	0.85252	0.85252	0.85252	0.91771
c_3	0	0	0	1
c_4	4	2	4	1
c_5	0	0	0	1
C_{1n}	0.5	0.5	0.5	0.75
C_{2n}	0.85252	1	0.65700	1
V_c (eV)	-104.37986	-33.80733	-96.78916	-39.09538
V_p (eV)	20.85777	10.19898	16.71820	13.45505
T (eV)	35.96751	9.49831	27.80371	12.74462
V_{at} (eV)	-17.98376	-4.74915	-13.90186	-6.37231
$E\|_{sO-sO}$ (eV)	0	-14.63489	0	-14.63489
$\Delta E_{H,sO}\|_{sO\ sO}$ (eV)	-2.26759	-1.85836	-2.89830	-2.26758
$E_\gamma\|_{sO\ sO}$ (eV)	2.26759	-12.77653	2.89830	-12.36731
$E_\gamma\|_{H,sO}$ (eV)	-63.27075	-31.63572	-63.27080	-31.63533
$E_T\left(atom-atom, nsp^2 AO\right)$ (eV)	-2.26759	-2.26759	-2.89830	0
$E_\gamma\|_{sO}$ (eV)	-65.53833	-33.90295	-66.16903	-31.63537
$\omega\left\{10^{15}\ rad/s\right\}$	15.4421	12.3131	10.3184	28.9084
E_K (eV)	10.16428	8.10471	6.79173	19.02803
E_D (eV)	-0.20668	-0.19095	-0.17058	-0.27301
E_{Kath} (eV)	0.17897 [6]	0.14829 [48]	0.08146 [41]	0.39427 [56]
E_{esc} (eV)	-0.11720	-0.11680	-0.12985	-0.07587
E_{inert} (eV)	0.14803	0.14803	0.14803	0.14803
$E_\gamma\|_{comp}$ (eV)	-65.77272	-34.01976	-66.42873	-31.71124
$E_{bilid}\|_{sO\ sO}$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{bilid}\|_{sO\ sO}$ (eV)	0	0	0	-13.59844
$E_{pl}\|_{comp}$ (eV)	7.23317	4.74998	7.88917	3.32988

Table 15.283. The total bond energies of thiophene calculated using the functional group composition and the energies of Table 15.282 compared to the experimental values [2].

Formula	Name	$C=C$	$C-C$	$C-S-C$	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_4H_4S	Thiophene	2	1	1	4	40.42501	40.430	0.00013

Table 15.284. The bond angle parameters of thiophene and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3.B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3.B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC_aS$	2.02241	3.25533	4.6030	-15.55033	3	-10.36001	S	0.87495 Eq. (15.65))	0.76144 (Eq. 15.126))	0.75	0.76144 (Eq. 15.126))	0.75	0.87495	0				119.58	119.9 (thiophene)
$\angle C_bC_aH_a$																119.58	115.84	124.58	
$\angle H_bC_bC_b$	2.02241	2.66807	4.1633	-16.68412 C_b	14	-15.95954 C_b	6	0.81549	0.85252	0.75	1	0.75	1.04540	0				124.58	124.3 (thiophene)
$\angle H_aC_aC_b$	2.02241	2.60925	4.1633	-16.68412 C_a	14	-15.95954 C_b	6	0.81549	0.85252	0.75	1	0.75	1.04540	0				127.57	
$\angle H_bC_bC_a$	2.02241	2.60925	4.0825	-17.09334 C_b	18	-16.68412 C_a	14	0.79597	0.81549	0.75	1	0.75	1.02453	0				123.13	
$\angle C_bC_bH_b$																123.13	113.60	123.27	124.3 (thiophene)
$\angle C_bC_aS$	2.60925	3.25533	4.9809	-17.81791 C_b	27	-10.36001	S	0.76360	0.65700 Eq. (15.153))	1	0.65700 Eq. (15.153))	1	0.71030	-0.72457				115.84	115.5 (thiophene)
$\angle C_aSC_a$	3.25533	3.25533	4.7958	-16.68412	14	-16.68412	14	0.81549	0.81549	1	1	1	0.81549	-1.85836				94.89	92.2 (thiophene)
$\angle C_aC_bC_b$	2.60925	2.66807	4.4159	-16.88873	15	-18.02252	29	0.80561	0.75493	1	1	1	0.78027	-1.85836				113.60	112.5 (thiophene)

IMIDAZOLE

Imidazole having the formula $C_3H_4N_2$ comprises a conjugated system that is equivalent to pyrrole with one of the conjugated CH groups replaced by a nitrogen atom. The CH, NH, and $C=C$ groups are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present. In addition, the nitrogen substitution creates a $C-N=C$ moiety comprising $C-N$ and $N=C$ functional groups. The $C-N$ bonding is the same as that of a tertiary amine except that the hybridization term c_2 in Eqs. (15.42) and (15.52) is that of the amino group of aniline, $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.152)). The hybridization factor provides double-bond character to match the group to the other orbitals of the molecule. $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)). This matches the energy of the group to that of the contiguous $N=C$ group wherein $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) per atom of the double bond with aromatic character as in the case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene, $n_1=2$ and C_2 and C_{2o} are the same as $C_2\left(benzeneC2sp^3HO\right)=0.85252$ (Eq. (15.143)) in Eqs. (15.42) and (15.52). To match the energy of the nitrogen to the $C2sp^3$ HO, c_2 of the $N=C$-bond MO is also given by Eq. (15.152). These parameters also provide an energy match to the $C-N-C$ group.

As in the case of pyrrole, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.152)) matches the double-bond character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2\left(benzeneC2sp^3HO\right)=0.85252$. Furthermore, $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 68. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.79-15.108) are given in Table 15.290.

Table 15.285. The symbols of functional groups of imidazole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	$C=C$
$N_b = C_c$ double bond	$N=C$
$C_b - N_b$	$C-N$
$C_a - N_a - C_c$	$C-N-C$
N_aH group	NH
CH	CH

Table 15.286. The geometrical bond parameters of imidazole and experimental values [1].

Parameter	$C=C$ Group	$N=C$ Group	$C-N$ Group	$C-N-C$ Group	NH Group	CH Group
$a\ (a_0)$	1.45103	1.44926	1.82450	1.43222	1.24428	1.53380
$c'\ (a_0)$	1.30463	1.30383	1.35074	1.29614	0.94134	1.01120
Bond Length $2c'\ (\AA)$	1.38076	1.37991	1.42956	1.37178	0.996270	1.07021
Exp. Bond Length $(\AA)$	1.382 (pyrrole)			1.370 (pyrrole)	0.996 (pyrrole)	1.076 (pyrrole)
$b,c\ (a_0)$	0.63517	0.63276	1.22650	0.60931	0.81370	1.15326
e	0.89910	0.89965	0.74033	0.90499	0.75653	0.65928

Table 15.287. The MO to HO intercept geometrical bond parameters of imidazole. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	r_{united} (a_0)	r_{final} (a_0)	$E_{C_{united}}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C'-H\ (C'_aH)$	C'_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1.10452	0.09331
$C'-H\ (C'_bH)$	C'_b	-1.13380	-0.46459	0	0	-153.21408	0.91771	0.82840	-16.42414	-16.23327	85.93	94.07	45.77	1.06995	0.05875
$C'-H\ (C'_cH)$	C'_c	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	84.49	95.51	44.47	1.08953	0.07833
$C'_a=(H)C'_b-N_b=C'_c$	C'_b	-0.46459	-1.13380	0	0	-153.21408	0.91771	0.82840	-16.42414	-16.23327	90.36	89.64	42.49	1.34547	0.00527
$C'_a=(H)C'_b-N_b=C'_c$	N_b	-0.46459	-0.92918	0	0		0.93084	0.83885	-16.21953		91.32	88.68	43.14	1.33135	0.01939
$C'_a=C'_b(H)N_b=C'_c$	C'_b	-1.13380	-0.46459	0	0	-153.21408	0.91771	0.82840	-16.42414	-16.23327	137.64	42.36	61.49	0.69250	0.61213
$HN_aC'_a=C'_b(H)$	C'_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	60.35	0.71784	0.58678
$C'_c(H)N_a-C'_a=C'_b(H)$	C'_a	-1.13380	-0.92918	0	0	-153.67867	0.91771	0.80561	-16.88873	-16.69786	138.54	41.46	61.09	0.69238	0.60376
$C'_c(H)N_a-C'_a=C'_b(H)$	N_a	-0.92918	-0.92918	0	0		0.93084	0.81549	-16.68411		138.92	41.08	61.59	0.68147	0.61467
$N-H\ (N_aH)$	N_a	-0.92918	-0.92918	0	0		0.93084	0.81549	-16.68411		117.34	62.66	62.90	0.56678	0.37456
$(H)C'_c-N_aC'_a=C'_b(H)$	C'_c	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	138.92	41.08	61.59	0.68147	0.61467
$C'_a=(H)C'_bN_b=C'_c$	C'_c	-0.92918	-0.92918	0	0	-153.47405	0.91771	0.81549	-16.68411	-16.49325	137.31	42.69	60.92	0.70446	0.59938
$C'_a=(H)C'_bN_b=C'_c$	N_b	-0.92918	-0.46459	0	0		0.93084	0.83885	-16.21953		138.20	41.80	62.08	0.67849	0.62534

Table 15.288. The energy parameters (eV) of functional groups of imidazole.

Parameters	$C=C$ Group	$N=C$ Group	$C-N$ Group	$C-N-C$ Group	NH Group	CH Group
n_1	2	2	1	2	1	1
n_2	0	0	0	0	0	0
n_3	0	0	0	0	0	0
C_1	0.5	0.5	0.5	0.5	0.75	0.75
C_2	0.85252	0.85252	1	0.85252	0.93613	1
c_1	1	1	1	1	0.75	1
c_2	0.85252	0.84665	0.84665	0.84665	0.92171	0.91771
c_3	0	0	0	0	1	1
c_4	4	4	2	4	1	1
c_5	0	0	0	0	1	1
C_{1n}	0.5	0.5	0.5	0.5	0.75	0.75
C_{2n}	0.85252	0.85252	1	0.85252	1	1
V_e (eV)	-104.37986	-103.92756	-32.44864	-106.58684	-39.48897	-39.09538
V_p (eV)	20.85777	20.87050	10.07285	20.99432	14.45367	13.45505
T (eV)	35.96751	35.85539	8.89248	37.21047	15.86820	12.74462
V_{ne} (eV)	-17.98376	-17.92770	-4.44624	-18.60523	-7.93410	-6.37231
$E(H_2O\ HO)$ (eV)	0	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_2NO}(H_2O\ HO)$ (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	-2.26758
$E_T(H_2O, HO)$ (eV)	2.26759	1.85836	-13.70571	3.71673	-14.53414	-12.36731
$E_T(H_2MO)$ (eV)	-63.27075	-63.27100	-31.63527	-63.27056	-31.63534	-31.63533
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	0
$E_T(MO)$ (eV)	-65.53833	-65.12910	-32.56455	-66.98746	-31.63537	-31.63537
$\omega\ (10^{15}\ rad/s)$	15.4421	15.4704	21.5213	15.7474	48.7771	28.9084
E_K (eV)	10.16428	10.18290	14.16571	10.36521	32.10594	19.02803
$\bar{E}_{ij}$ (eV)	-0.20668	-0.20558	-0.24248	-0.21333	-0.35462	-0.27301
$\bar{E}_{Kmb}$ (eV)	0.17897 [6]	0.20768 [58]	0.12944 [23]	0.11159 [12]	0.40696 [24]	0.39427 [56]
$\bar{E}_{nne}$ (eV)	-0.11720	-0.10174	-0.17775	-0.15754	-0.15115	-0.07587
E_{nne} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(fcmp)$ (eV)	-65.77272	-65.33259	-32.74230	-67.30254	-31.78651	-31.71124
$E_{initial}(e_1, HO\ HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{initial}(e_2, HO\ HO)$ (eV)	0	0	0	0	-13.59844	-13.59844
$E_D(fcmp)$ (eV)	7.23317	6.79303	3.47253	8.76298	3.51208	3.32988

Table 15.289. The total bond energies of imidazole calculated using the functional group composition and the energies of Table 15.288 compared to the experimental values [2].

Formula	Name	$C=C$	$N=C$	$C-N$	$C-N-C$	NH	CH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_3H_4N_2$	Imidazole	1	1	1	1	1	3	39.76343	39.74106	-0.00056

Table 15.290. The bond angle parameters of imidazole and experimental values [59]. In the calculation of θ_{e_1}, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{C'_{coulombic}}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{C'_{coulombic}}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C'_1	C'_2	c_1	c'_2	E_T (eV)	θ_e (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HC'_aN_a$	2.02241	2.59228	4.0166	-14.82575	1	-14.53414	N	0.91771	0.92171 Eq. (15.151))	0.75	1	0.75	1.00435	0				120.51	117.4 (imidazole)
$\angle C'_bC'_dH_d$																120.51	106.63	132.86	136.3 (imidazole)
$\angle HN_aC'_a$	1.88268	2.59228	3.8987	-14.53414	N	-16.49325	13	0.84665 (Eq. (15.151))	0.82493 (Eq. (15.64))	0.75	1	0.75	0.97435	0				120.37	122.9 (imidazole)
$\angle H_aC'_aC'_b$	2.02241	2.60925	4.2895	-16.88873 C'_a	15	-15.75493 C'_b	4	0.80561	0.86359	0.75	1	0.75	1.07196	0				135.30	136.3 (imidazole)
$\angle H_bC'_bC'_a$	2.02241	2.60925	4.2740	-15.95954 C'_b	6	-14.82575 C'_a	1	0.85252	0.91771	0.75	1	0.75	1.07647	0				134.28	133.2 (imidazole)
$\angle N_bC'_bH_b$																134.28	111.18	114.54	115.8 (imidazole)
$\angle H_cC'_cN_a$	2.02241	2.59228	3.8471	-15.95954 C'_c	6	-14.53414	N	0.87495	0.84665 (Eq. (15.152))	0.75	1	0.75	0.96765					112.37	110.4 (imidazole)
$\angle N_bC'_cH_c$																112.37	109.83	137.80	138.2 (imidazole)
$\angle HN_aC'_c$	1.88268	2.59228	4.0661	-14.53414	N	-15.76868	6	0.84665 (Eq. (15.151))	0.86284 (Eq. (15.64))	0.75	1	0.75	1.01912	0				129.96	129.1 (imidazole)
$\angle N_aC'_aC'_b$	2.59228	2.60925	4.1952	-14.53414	N	-17.09334 C'_b	18	0.84665 (Eq. (15.152))	0.79597	1	1	1	0.82131	-1.44915				107.52	106.3 (imidazole)
$\angle C'_aN_aC'_c$	2.59228	2.59228	4.2426	-17.81791	26	-17.81791	26	0.76360	0.76360	1	1	1	0.76360	-1.85836				109.83	107.2 (imidazole)
$\angle C'_cN_bC'_b$	2.60766	2.70148	4.3128	-17.61330	23	-17.61330	25	0.77247	0.77247	1	1	1	0.77247	-1.85836				108.64	105.4 (imidazole)
$\angle C'_aC'_bN_b$	2.60925	2.70148	4.3818	-15.95955	6	-14.53414	N	0.85252	0.84665 (Eq. (15.152))	1	1	1	0.84958	-1.85836				111.18	109.8 (imidazole)
$\angle N_aC'_cN_b$	2.59228	2.60766	4.2544	-16.68411	13	-16.21953	8	0.81549	0.83885	1	1	1	0.82717	-1.44915				109.80	111.3 (imidazole)

PYRIDINE

Pyridine has the formula C_5H_5N and comprises the benzene molecule with one CH group replaced by a nitrogen atom which gives rise to a $\overset{3e}{C=N}$ functional group. The aromatic $\overset{3e}{C=C}$ and $C-H$ functional groups are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $\overset{3e}{C=N}$ group which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine $C2sp^3$ HO initially has four unpaired electrons. Each $C-H$ bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. In pyridine the three $N2p$ electrons are donated to the aromatic bond. Thus, as in the case of the $\overset{3e}{C=C}$ group, each $\overset{3e}{C=N}$ bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the $C2sp^3$ HO and the $N2p$ AO of the participating carbon and nitrogen atoms, respectively.

The solution of the $\overset{3e}{C=N}$ functional group comprises the hybridization of the $2s$ and $2p$ AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The $\overset{3e}{C=N}$-bond MO is solved as a double bond with $n_1=2$ in Eqs. (15.42) and (15.147). The hybridization factor $c_2\left(C2sp^3 HO\ to\ N\right)=0.91140$ (Eq. (15.116)) matches the double-bond character of the $C2sp^3$ HO to the N atom, and C_2 and C_{2a} in Eqs. (15.42) and (15.147) are also given by Eq. (15.116) in order to match the nitrogen to the aromatic $C2sp^3$ HO such that $\Delta E_{H_2MO}\left(AO/HO\right)=0$ in Eq. (15.42). Furthermore, $E_T\left(atom-atom,msp^3.AO\right)$ of the $\overset{3e}{C=N}$-bond MO in Eq. (15.147) due to the charge donation from the C and N atoms to the MO is $-1.44915\,eV$ corresponding to an energy contribution from each atom that is equivalent to that of an independent methyl group, $-0.72457\,eV$ (Eq. (14.151)). The contributions are also the same as those for a primary amine group as given in the corresponding section. As in the case of benzene, the aromatic $E_T(Group)$ and $E_D(Group)$ are

given by Eqs. (15.146) and (15.147), respectively, with $f_1 = 0.75$. The breakage of the CNC bonds results in three unpaired electrons on the N atom. Thus, the corresponding E_{mag} given by Eq. (15.60) was normalized for the two bonds per atom and for $f_1 = 0.75$ and was subtracted from the total energy of the $C\overset{3e}{=}N$-bond MO in Eq. (15.147). The pyridine vibrational energies are similar to those of benzene [60]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.79-15.108) are given in Table 15.296.

Table 15.291. The symbols of functional groups of pyridine.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH
$C_a\overset{3e}{=}N$	$C\overset{3e}{=}N$

Table 15.292. The geometrical bond parameters of pyridine and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	CH Group	$C\overset{3e}{=}N$ Group
$a\ (a_0)$	1.47348	1.60061	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.27073
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.34489
Exp. Bond Length $(\AA)$	1.394 (pyridine)	1.084 (pyridine)	1.340 (pyridine)
$b,c\ (a_0)$	0.66540	1.22265	0.74237
e	0.89223	0.64537	0.86345

Table 15.293. The MO to HO intercept geometrical bond parameters of pyridine. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Confined}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\ (a_0)$	$d_2\ (a_0)$
$C-H\ (C_aH)$	C_a	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H\ (C_bH)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$(H)C_b(H)C_a\overset{3e}{=}NC_a$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$(H)C_b(H)C_a\overset{3e}{=}NC_a$	N	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$(H)C_b\overset{3e}{=}C_a(H)N$	C_a	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)C_b\overset{3e}{=}C_a(H)N$ $(H)C_b\overset{3e}{=}C_b(H)C_a(H)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.294. The energy parameters (eV) of functional groups of pyridine.

Parameters	$C{=}C$ Group	CH Group	$C{=}N$ Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
c_1	1	1	1
c_2	0.85252	0.91771	0.91140
c_3	0	1	0
c_4	3	1	3
c_5	0	1	0
$C_{1\sigma}$	0.5	0.75	0.5
$C_{2\sigma}$	0.85252	1	0.91140
V_e (eV)	-101.12679	-37.10024	-102.01431
V_p (eV)	20.69825	13.17125	21.41410
T (eV)	34.31559	11.58941	34.65890
V_{en} (eV)	-17.15779	-5.79470	-17.32945
$E(\sigma\text{-}\pi\sigma)$ (eV)	0	-14.63489	0
$\Delta E_{H_2\sigma}(\sigma\pi\sigma)$ (eV)	0	-1.13379	0
$E_T(\sigma\pi\sigma)$ (eV)	0	-13.50110	0
$E_T(H_2\sigma)$ (eV)	-63.27075	-31.63539	-63.27076
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-1.44915
$E_T(\sigma\pi)$ (eV)	-65.53833	-32.20226	-64.71988
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	43.6311
E_K (eV)	32.73133	17.43132	28.71875
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.33540
$\bar{E}_{AvB}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]
$\bar{E}_{esc}$ (eV)	-0.25982	-0.08364	-0.23715
E_{ang} (eV)	0.14803	0.14803	0.09457
$E_T(\text{fitting})$ (eV)	-49.54347	-32.28590	-48.82472
$E_{united}(\sigma_1,\sigma\pi\sigma)$ (eV)	-14.63489	-14.63489	-14.63489
$E_{united}(\sigma_1,\sigma\pi\sigma)$ (eV)	0	-13.59844	0
$E_D(\text{fitting})$ (eV)	5.63881	3.90454	4.92005

Table 15.295. The total bond energies of pyridine calculated using the functional group composition and the energies of Table 15.294 compared to the experimental values [2].].

Formula	Name	$C=C$	CH	$C=N$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_5H_5N	Pyridine	4	5	2	51.91802	51.87927	-0.00075

Table 15.296. The bond angle parameters of pyridine and experimental values [1]. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle HC_aN$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116))	0.75	1	0.75	0.99312	0				117.65	115.9 (pyridine)
$\angle NC_aC_b$	2.54147	2.62936	4.5607	-14.53414	N	-16.52644 C_b	12	0.91140 Eq (15.116))	0.82327	1	1	1	0.86734	-1.44915				123.76	123.9 (pyridine)
$\angle C_aNC_a$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	0.76801	-1.85836				117.09	116.8 (pyridine)

PYRIMIDINE

Pyrimidine has the formula $C_4H_4N_2$ and comprises the pyridine molecule with one additional CH group replaced by a nitrogen atom which gives rise to a second $\overset{3e}{C=N}$ functional group that is equivalent to that of pyridine given in the corresponding section. The aromatic $\overset{3e}{C=C}$ and $C-H$ functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $\overset{3e}{C=N}$ group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 70. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.79-15.108) are given in Table 15.302.

Table 15.297. The symbols of functional groups of pyrimidine.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH
$C_{a,b,d}\overset{3e}{=}N$	$\overset{3e}{C=N}$

Table 15.298. The geometrical bond parameters of pyrimidine and experimental values [1].

Parameter	$C^{3e}=C$ Group	$C'H$ Group	$C^{3e}=N$ Group
$a\ (a_0)$	1.47348	1.60061	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.27073
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.34489
Exp. Bond Length $(\AA)$	1.393 (pyrimidine)	1.084 (pyridine)	1.340 (pyrimidine)
$b,c\ (a_0)$	0.66540	1.22265	0.74237
e	0.89223	0.64537	0.86345

Table 15.299. The MO to HO intercept geometrical bond parameters of pyrimidine. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{C\text{-}bond}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	78.27	101.73	41.39	1.20084	0.16785
$C-H\ (C_{b,d}H)$	C_b C_d	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H\ (C_cH)$	C_c	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$(H)C_c(H)C_b=^{3e}N_bC_a$ $(H)C_c(H)C_d=^{3e}N_aC_a$	C_b C_d	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$(H)C_c(H)C_b=^{3e}N_bC_a$ $(H)C_c(H)C_d=^{3e}N_aC_a$	N_b N_a	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$(H)C_c(H)C_bN_b=^{3e}C_a(H)$ $(H)C_c(H)C_dN_a=^{3e}C_a(H)$	C_a	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	129.26	50.74	59.44	0.74824	0.52249
$(H)C_c(H)C_bN_b=^{3e}C_a(H)$ $(H)C_c(H)C_dN_a=^{3e}C_a(H)$	N_b N_a	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$N_a(H)C_d=^{3e}C_c(H)C_b$ $N_b(H)C_b=^{3e}C_c(H)C_d$	C_c	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$N_a(H)C_d=^{3e}C_c(H)C_b$ $N_b(H)C_b=^{3e}C_c(H)C_d$	C_b C_d	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165

Table 15.300. The energy parameters (eV) of functional groups of pyrimidine.

Parameters	$C^{3e}=C$ Group	CH Group	$C^{3e}=N$ Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
c_1	1	1	1
c_2	0.85252	0.91771	0.91140
c_3	0	1	0
c_4	3	1	3
c_5	0	1	0
$C_{1\pi}$	0.5	0.75	0.5
$C_{2\pi}$	0.85252	1	0.91140
V_e (eV)	-101.12679	-37.10024	-102.01431
V_p (eV)	20.69825	13.17125	21.41410
T (eV)	34.31559	11.58941	34.65890
V_M (eV)	-17.15779	-5.79470	-17.32945
$E(\pi\text{-}no\ \pi o)$ (eV)	0	-14.63489	0
$\Delta E_{\pi_2\pi o}(\pi\text{-}no\ \pi o)$ (eV)	0	-1.13379	0
$E_\gamma(\pi\text{-}no\ \pi o)$ (eV)	0	-13.50110	0
$E_\gamma(\pi_2\pi o)$ (eV)	-63.27075	-31.63539	-63.27076
$E_\gamma\left(atom-atom,msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-1.44915
$E_\gamma(\pi o)$ (eV)	-65.53833	-32.20226	-64.71988
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	43.6311
E_K (eV)	32.73133	17.43132	28.71875
$\overline{E}_D$ (eV)	-0.35806	-0.26130	-0.33540
$\overline{E}_{Kek}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]
$\overline{E}_{ove}$ (eV)	-0.25982	-0.08364	-0.23715
E_{mag} (eV)	0.14803	0.14803	0.09457
$E_\gamma(Group)$ (eV)	-49.54347	-32.28590	-48.82472
$E_{unbal}(\pi_1\text{-}no\ \pi o)$ (eV)	-14.63489	-14.63489	-14.63489
$E_{unbal}(\pi_1\text{-}no\ \pi o)$ (eV)	0	-13.59844	0
$E_D(Group)$ (eV)	5.63881	3.90454	4.92005

Table 15.301. The total bond energies of pyrimidine calculated using the functional group composition and the energies of Table 15.300 compared to the experimental values [2].].

Formula	Name	$C^{3r}=C$	CH	$C^{3r}=N$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_4N_2$	Pyrimidine	2	4	4	46.57597	46.51794	-0.00125

Table 15.302. The bond angle parameters of pyrimidine and experimental values [1]. E_T is $E_T\left(atom-atom,nsp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5385	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle HCN$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116))	0.75	1	0.75	0.99312	0				117.65	115.9 (pyridine)
$\angle NCC$	2.54147	2.62936	4.5607	-14.53414	N	-16.52644	13	0.91140 Eq. (15.116))	0.82327	1	1	1	0.86734	-1.44915				123.76	123.9 (pyridine)
$\angle CNC$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	0.76801	-1.85836				117.09	115.5 (pyrimidine)
$\angle NCN$	2.54147	2.54147	4.5826	-15.55033	3	-15.55033	3	0.87495	0.87495	1	1	1	0.87495	-1.85836				128.73	127.6 (pyrimidine)

PYRAZINE

Pyrazine has the formula $C_4H_4N_2$ and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The $C\overset{3e}{=}N$ functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 71. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrazine determined using Eqs. (15.79-15.108) are given in Table 15.308.

Table 15.303. The symbols of functional groups of pyrazine.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH
$C_a\overset{3e}{=}N$	$C\overset{3e}{=}N$

Table 15.304. The geometrical bond parameters of pyrazine and experimental values [1].

Parameter	$C \overset{3e}{=} C$ Group	CH Group	$C \overset{3e}{=} N$ Group
$a\ (a_0)$	1.47348	1.60061	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.27073
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.34489
Exp. Bond Length $(\AA)$	1.339 (pyrazine)	1.115 (pyrazine)	1.403 (pyrazine)
$h,c\ (a_0)$	0.66540	1.22265	0.74237
e	0.89223	0.64537	0.86345

Table 15.305. The MO to HO intercept geometrical bond parameters of pyrazine. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	r_{mutual} (a_0)	r_{final} (a_0)	$E_{C_{valence}}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-0.54343	-0.85035	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$(H)C_a(H)C_a \overset{3e}{=} NC_a$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$(H)C_a(H)C_a \overset{3e}{=} NC_a$	N	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$N(H)C_a \overset{3e}{=} C_a(H)N$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165

Table 15.306. The energy parameters (eV) of functional groups of pyrazine.

Parameters	$C^{3e}=C$ Group	CH Group	$C^{3e}=N$ Group
f_1	0.75	1	0.75
n_1	2	1	2
n_2	0	0	0
n_3	0	0	0
C_1	0.5	0.75	0.5
C_2	0.85252	1	0.91140
c_1	1	1	1
c_2	0.85252	0.91771	0.91140
c_3	0	1	0
c_4	3	1	3
c_5	0	1	0
C_{1o}	0.5	0.75	0.5
C_{2o}	0.85252	1	0.91140
V_s (eV)	-101.12679	-37.10024	-102.01431
V_p (eV)	20.69825	13.17125	21.41410
T' (eV)	34.31559	11.58941	34.65890
V_{pi} (eV)	-17.15779	-5.79470	-17.32945
$E(AO\ HO)$ (eV)	0	-14.63489	0
$\Delta E_{H_2,MO}(AO\ HO)$ (eV)	0	-1.13379	0
$E_T(AO\ HO)$ (eV)	0	-13.50110	0
$E_T(H_2,MO)$ (eV)	-63.27075	-31.63539	-63.27076
$E_T\left(atom-atom,msp^3.AO\right)$ (eV)	-2.26759	-0.56690	-1.44915
$E_T(MO)$ (eV)	-65.53833	-32.20226	-64.71988
$\omega\ \left(10^{15}\ rad/s\right)$	49.7272	26.4826	43.6311
E_K (eV)	32.73133	17.43132	28.71875
E_D (eV)	-0.35806	-0.26130	-0.33540
E_{Kroh} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]
E_{rep} (eV)	-0.25982	-0.08364	-0.23715
E_{mag} (eV)	0.14803	0.14803	0.09457
$E_T(trunp)$ (eV)	-49.54347	-32.28590	-48.82472
$E_{antibond}(\sigma_1,AO\ HO)$ (eV)	-14.63489	-14.63489	-14.63489
$E_{antibond}(\sigma_2,AO\ HO)$ (eV)	0	-13.59844	0
$E_{p_\pi}(trunp)$ (eV)	5.63881	3.90454	4.92005

Table 15.307. The total bond energies of pyrazine calculated using the functional group composition and the energies of Table 15.306 compared to the experimental values [2].].

Formula	Name	$C=C^{3e}$	CH	$C=N^{3e}$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_4N_2$	Pyrazine	2	4	4	46.57597	46.51380	0.00095

Table 15.308. The bond angle parameters of pyrazine and experimental values [1]. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombe}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombe}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_r (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene) 121.3 (pyridine)
$\angle HC'N$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116))	0.75	1	0.75	0.99312	0				117.65	115.9 (pyridine)
$\angle CCH$																117.65	116.81	125.54	123.9 (pyrazine)
$\angle NCC$	2.54147	2.62936	4.4045	-14.53414	N	-17.09334	7	0.91140 Eq. (15.116))	0.79597	1	1	1	0.85368	-1.44915				116.81	115.6 (pyrazine
$\angle CNC$	2.54147	2.54147	4.3359	-17.71560	24	-17.71560	24	0.76801	0.76801	1	1	1	0.76801	-1.85836				117.09	116.8 (pyrimidine)

QUINOLINE

Quinoline has the formula C_9H_7N and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a $\overset{3e}{C=N}$ functional group. The aromatic $\overset{3e}{C=C}$ and $C-H$ functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the $\overset{3e}{C=N}$ group which is also aromatic. The $C-C$ functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the $\overset{3e}{C=N}$ group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 72. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.79-15.108) are given in Table 15.314.

Table 15.309. The symbols of functional groups of quinoline.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C=C}$
CH (aromatic)	CH
C_h-C_h (bridging bond)	$C-C$
$C_{a,d}\overset{3e}{=}N$	$\overset{3e}{C=N}$

Table 15.310. The geometrical bond parameters of quinoline and experimental values [1].

Parameter	$C\overset{3e}{=}C$ Group	CH Group	$C-C$ Group	$C\overset{3e}{=}N$ Group
$a\ (a_0)$	1.47348	1.60061	1.75607	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.32517	1.27073
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.40250	1.34489
Exp. Bond Length $(\AA)$	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
$h,c\ (a_0)$	0.66540	1.22265	1.15226	0.74237
e	0.89223	0.64537	0.75462	0.86345

Table 15.311. The MO to HO intercept geometrical bond parameters of quinoline. E_T is $E_T(atom-atom, msp^3.AO)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Conbond}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_a H)$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H\ (C_b H)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$N(H)C_a\overset{3e}{=}C_b(H)$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)C_b\overset{3e}{=}C_{a,b,c,d}(H)$	C_b	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$(H)C_b(C_d)C_c\overset{3e}{=}C_b$	C_c	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57038
$N(C_c)C_d\overset{3e}{=}C_b$	C_d	-0.85035	-0.54343	-0.28345	0	-153.29292	0.91771	0.82445	-16.50298	-16.31211	135.42	44.58	60.42	0.72743	0.58725
$C_b(H)C_a\overset{3e}{=}N$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$C_b(H)C_a\overset{3e}{=}N$ $C_b(C_c)C_d\overset{3e}{=}N$	N	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$C_b(C_c)C_d\overset{3e}{=}N$	C_d	-0.85035	-0.54343	-0.28345	0	-153.29291	0.91771	0.82445	-16.50297	-16.31211	129.21	50.79	59.38	0.74960	0.52113
$\left((H)C_b\overset{3e}{=}\right)_2 C_c-C_d$	C_c	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	95.01	84.99	44.41	1.25451	0.07066
$N(C_b)C_d-C_c$	C_d	-0.85035	-0.54343	-0.28345	0	-153.29292	0.91771	0.82445	-16.50298	-16.31211	96.31	83.69	45.33	1.23456	0.09061

Table 15.312. The energy parameters (eV) of functional groups of quinoline.

Parameters	$C^{3e}=C$ Group	CH Group	$C-C$ Group	$C^{3e}=N$ Group
f_1	0.75	1	1	0.75
n_1	2	1	1	2
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	1	0.91140
c_1	1	1	1	1
c_2	0.85252	0.91771	0.85252	0.91140
c_3	0	1	0	0
c_4	3	1	2	3
c_5	0	1	0	0
C_{1o}	0.5	0.75	0.5	0.5
C_{2o}	0.85252	1	1	0.91140
V_s (eV)	-101.12679	-37.10024	-34.43791	-102.01431
V_p (eV)	20.69825	13.17125	10.26723	21.41410
T (eV)	34.31559	11.58941	9.80539	34.65890
V_{ss} (eV)	-17.15779	-5.79470	-4.90270	-17.32945
$E(sp^3\ HO)$ (eV)	0	-14.63489	-14.63489	0
$\Delta E_{H_2O}(sp^3\ HO)$ (eV)	0	-1.13379	-1.13379	0
$E_T(sp^3\ HO)$ (eV)	0	-13.50110	-13.50110	0
$E_T(H_2O)$ (eV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.56690	-1.44915
$E_T(HO)$ (eV)	-65.53833	-32.20226	-32.20226	-64.71988
$\omega\ (10^{15}\ rad/s)$	49.7272	26.4826	23.6343	43.6311
E_K (eV)	32.73133	17.43132	15.55648	28.71875
E_D (eV)	-0.35806	-0.26130	-0.25127	-0.33540
E_{Kinh} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]	0.19649 [49]
E_{osc} (eV)	-0.25982	-0.08364	-0.18971	-0.23715
E_{magn} (eV)	0.14803	0.14803	0.14803	0.09457
$E_T(Group)$ (eV)	-49.54347	-32.28590	-32.39198	-48.82472
$E_{mmol}(c_1\ sp^3\ HO)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{mmol}(c_4\ sp^3\ HO)$ (eV)	0	-13.59844	0	0
$E_D(Group)$ (eV)	5.63881	3.90454	3.12220	4.92005

Table 15.313. The total bond energies of quinoline calculated using the functional group composition and the energies of Table 15.312 compared to the experimental values [2].].

Formula	Name	$C^{3e}=C$	CH	$C-C$ Group	$C^{3e}=N$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_9H_7N	Quinoline	8	7	1	2	85.40453	85.48607	0.00178

Table 15.314. The bond angle parameters of quinoline and experimental values [1]. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$	2.62936	2.65034	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				119.40	119.4 (naphthalene)
$\angle CCH$																119.40		120.30	
$\angle C_dNC_a$	2.54147	2.54147	4.3818	-17.43216	22	-17.71560	24	0.78050	0.76801	1	1	1	0.77426	-1.85836				119.10	

ISOQUINOLINE

Isoquinoline has the formula C_9H_7N and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a $C\overset{3e}{=}N$ functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the $C\overset{3e}{=}N$ group which is also aromatic. The $C-C$ functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the $C\overset{3e}{=}N$ group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 73. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of isoquinoline are given in Tables 15.316, 15.317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each $E_D(_{Group})$ of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.79-15.108) are given in Table 15.320.

Table 15.315. The symbols of functional groups of isoquinoline.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH
C_b-C_b (bridging bond)	$C-C$
$C_{a,d}\overset{3e}{=}N$	$C\overset{3e}{=}N$

Table 15.316. The geometrical bond parameters of isoquinoline and experimental values [1].

Parameter	$C \overset{3e}{=} C$ Group	CH Group	$C-C$ Group	$C \overset{3e}{=} N$ Group
$a\ (a_0)$	1.47348	1.60061	1.75607	1.47169
$c'\ (a_0)$	1.31468	1.03299	1.32517	1.27073
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.40250	1.34489
Exp. Bond Length $(\AA)$	1.40 (avg.) (naphthalene)	1.101 (benzene)	1.42 (naphthalene)	1.340 (pyridine)
$h,c\ (a_0)$	0.66540	1.22265	1.15226	0.74237
e	0.89223	0.64537	0.75462	0.86345

Table 15.317. The MO to HO intercept geometrical bond parameters of isoquinoline. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}\ (a_0)$	$r_{final}\ (a_0)$	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' (°)	θ_1 (°)	θ_2 (°)	$d_1\ (a_0)$	$d_2\ (a_0)$
$C-H\ (C_aH)$	C_a	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H\ (C_bH)$	C_b	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	76.35	103.65	40.11	1.22423	0.19124
$C-H\ (C_eH)$	C_e	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$N(H)C_a \overset{3e}{=} C_d$ $N(H)C_b \overset{3e}{=} C_e$	C_a C_b	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)C_e \overset{3e}{=} C_{b,c,d}(H)$	C_e	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$(H)C_e(C_d)C_d \overset{3e}{=} C_{a,c}$	C_d	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	134.81	45.19	59.66	0.74430	0.57038
$C_d(H)C_a \overset{3e}{=} N$ $C_e(H)C_b \overset{3e}{=} N$	C_a C_b	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$C_d(H)C_a \overset{3e}{=} N$ $C_e(H)C_b \overset{3e}{=} N$	N	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$C_{a,c}(C_e)C_d - C_d$	C_d	-0.85035	-0.85035	-0.28345	0	-153.59983	0.91771	0.80939	-16.80989	-16.61903	95.01	84.99	44.41	1.25451	0.07066

Table 15.318. The energy parameters (eV) of functional groups of isoquinoline.

Parameters	$C^{3r}=C$ Group	CH Group	$C-C$ Group	$C^{3e}=N$ Group
f_1	0.75	1	1	0.75
n_1	2	1	1	2
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.5
C_2	0.85252	1	1	0.91140
c_1	1	1	1	1
c_2	0.85252	0.91771	0.85252	0.91140
c_3	0	1	0	0
c_4	3	1	2	3
c_5	0	1	0	0
$C_{1\sigma}$	0.5	0.75	0.5	0.5
$C_{2\sigma}$	0.85252	1	1	0.91140
V_e (eV)	-101.12679	-37.10024	-34.43791	-102.01431
V_n (eV)	20.69825	13.17125	10.26723	21.41410
T (eV)	34.31559	11.58941	9.80539	34.65890
V_m (eV)	-17.15779	-5.79470	-4.90270	-17.32945
$E(\sigma\ no)$ (eV)	0	-14.63489	-14.63489	0
$\Delta E_{H_2\sigma}(\sigma\ no)$ (eV)	0	-1.13379	-1.13379	0
$E_T(\sigma\ no)$ (eV)	0	-13.50110	-13.50110	0
$E_T(H_2\sigma)$ (eV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_T(atom-atom,msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.56690	-1.44915
$E_T(\sigma)$ (eV)	-65.53833	-32.20226	-32.20226	-64.71988
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	23.6343	43.6311
E_K (eV)	32.73133	17.43132	15.55648	28.71875
$\bar{E}_D$ (eV)	-0.35806	-0.26130	-0.25127	-0.33540
$\bar{E}_{Kmb}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]	0.19649 [49]
$\bar{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.18971	-0.23715
E_{mag} (eV)	0.14803	0.14803	0.14803	0.09457
$E_T(Group)$ (eV)	-49.54347	-32.28590	-32.39198	-48.82472
$E_{emiss}(\sigma_1\ no\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{emiss}(\sigma_2\ no\ no)$ (eV)	0	-13.59844	0	0
$E_{Tb}(Group)$ (eV)	5.63881	3.90454	3.12220	4.92005

Table 15.319. The total bond energies of isoquinoline calculated using the functional group composition and the energies of Table 15.318 compared to the experimental values [2].].

Formula	Name	$C^{3e}=C$	CH	$C-C$ Group	$C^{3e}=N$ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_9H_7N	Isoquinoline	8	7	1	2	85.40453	85.44358	0.00046

Table 15.320. The bond angle parameters of isoquinoline and experimental values [1]. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$	2.62936	2.65034	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				119.40	119.4 (naphthalene)
$\angle CCH$																119.40		120.30	
$\angle C_pNC_h$	2.54147	2.54147	4.3818	-17.43216	22	-17.71560	24	0.78050	0.76801	1	1	1	0.77426	-1.85836				119.10	

INDOLE

Indole having the formula C_8H_7N comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 74. The aromatic $C\overset{3e}{=}C$ and $C-H$ functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The CH, NH, and $C_d=C_e$ groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The C_b-C_d single bond of aryl carbon to the $C_d=C_e$ bond is also a functional group. This group is equivalent to the $C-C(O)$ group of benzoic acids with regard to $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) both being $-1.29147\,eV$. This energy is a linear combination of $\frac{-1.13379\,eV}{2}$, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-H$ group that the C_b-C_d and $C-C(O)$ groups replace, and that of an independent $C2sp^3$ HO, $-0.72457\,eV$ (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term c_2 is the aromatic $c_2\left(benzeneC2sp^3HO\right)=0.85252$ to match the aryl $C2sp^3$ HO, and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the $C-N-C$-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1=2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2\left(arylC2sp^3HO\ to\ N\right)=0.84665$ (Eq. (15.152)) matches the aromatic character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2\left(benzeneC2sp^3HO\right)=0.85252$. Furthermore, $\Delta E_{H_2MO}\left(AO/HO\right)$ in Eq. (15.42) and $E_T\left(atom-atom,msp^3.AO\right)$ in Eq. (15.52) are both $-2.42526\,eV$ which is a linear combination of $\frac{-1.13379\,eV}{2}$, $E_T\left(atom-atom,msp^3.AO\right)$ of the $C-H$ group that the C_c-N bond replaces, and $-1.85836\,eV$ (Eq. (14.513)) which is equivalent to the corresponding component of the $C-N-C$-bond of pyrrole.

The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.79-15.108) are given in Table 15.326.

Table 15.321. The symbols of functional groups of indole.

Functional Group	Group Symbol
CC (aromatic bond)	$\overset{3e}{C}=C$
CH (aromatic)	CH (i)
$C_d = C_e$ double bond	$C=C$
$C_b - C_d$	$C-C$
CH	CH (ii)
$C_c - N - C_e$	$C-N-C$
NH group	NH

Table 15.322. The geometrical bond parameters of indole and experimental values [1].

Parameter	$C^{3e}=C$ Group	CH (i) Group	$C=C$ Group	CH (ii) Group	$C-C$ Group	$C-N-C$ Group	NH Group
$a\ (a_0)$	1.47348	1.60061	1.45103	1.53380	1.81395	1.44394	1.24428
$c'\ (a_0)$	1.31468	1.03299	1.30463	1.01120	1.34683	1.30144	0.94134
Bond Length $2c'\ (\AA)$	1.39140	1.09327	1.38076	1.07021	1.42542	1.37738	0.996270
Exp. Bond Length $(\AA)$	1.399 (benzene)	1.101 (benzene)	1.382 (pyrrole)	1.076 (pyrrole	1.417 (pyrrole)	1.370 (pyrrole)	0.996 (pyrrole)
$b,c\ (a_0)$	0.66540	1.22265	0.63517	1.15326	1.21510	0.62548	0.81370
e	0.89223	0.64537	0.89910	0.65928	0.74248	0.90131	0.75653

Table 15.323. The MO to HO intercept geometrical bond parameters of indole. R_1 is an alkyl group and R,R',R'' are H or alkyl groups. E_T is $E_T\left(atom-atom,msp^3,AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Coulomb}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ' $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C-H\ (C_aH)$	C_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C_a^{3e}=HC_a^{3e}=C_{a,b,c}$	C_a	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
$C_a^{3e}=(C_d)C_b^{3e}=C_c$ $C_c^{3e}=(C_d)C_b^{3e}=C_a$	C_b	-0.85035	-0.64574	-0.85035	0	-153.96212	0.91771	0.79232	-17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124
$C_a^{3e}=C_c(N)C_b$ $C_b^{3e}=C_c(N)C_a$	C_c	-0.60631	-0.85035	-0.85035	0	-153.92270	0.91771	0.79414	-17.13276	-16.94190	134.16	45.84	58.89	0.76140	0.55328
$C_a(H)C_b-C_d(H)C_e$	C_b	-0.85035	-0.85035	-0.64574	0	-153.96212	0.91771	0.79232	-17.17218	-16.98132	87.89	92.11	40.66	1.37597	0.02914
$C_a(H)C_b-C_d(H)C_e$	C_d	-0.64574	-1.13379	0	0	-153.39522	0.91771	0.81937	-16.60528	-16.41442	90.51	89.49	42.40	1.33953	0.00729
$C_b(H)C_d=C_eN$	C_d	-0.64574	-1.13379	0	0	-153.39522	0.91771	0.81937	-16.60528	-16.41442	137.29	42.71	61.04	0.70255	0.60208
$C_b(H)C_d=C_eN$	C_e	-1.13379	-0.60631	0	0	-153.35580	0.91771	0.82132	-16.56586	-16.37500	137.37	42.63	61.14	0.70038	0.60425
$C_dC_e-NC_e$	C_e	-1.13379	-0.60631	0	0	-153.35580	0.91771	0.82132	-16.56586	-16.37500	138.03	41.97	61.42	0.69080	0.61064
$C_dC_a-NC_e$ $C_aC_c-NC_e$	N	-0.60631	-0.60631	0	0		0.93084	0.84833	-16.03838		139.04	40.96	62.76	0.66083	0.64061
$N-H\ (NH)$	N	-0.60631	-0.60631	0	0		0.93084	0.84833	-16.03838		119.52	60.48	65.13	0.52338	0.41796
$C_aC_c-NC_e$	C_c	-0.85035	-0.85035	-0.60631	0	-153.92269	0.91771	0.79414	-17.13276	-16.94189	136.97	43.03	60.05	0.72095	0.58048

Table 15.324. The energy parameters (eV) of functional groups of indole.

Parameters	$C^{3e}=C$ Group	CH (i) Group	$C=C$ Group	$C-C$ Group	CH (ii) Group	$C-N-C$ Group	NH Group
f_1	0.75	1	1	1	1	1	1
n_1	2	1	2	1	1	2	1
n_2	0	0	0	0	0	0	0
n_3	0	0	0	0	0	0	0
C_1	0.5	0.75	0.5	0.5	0.75	0.5	0.75
C_2	0.85252	1	0.85252	1	1	0.85252	0.93613
c_1	1	1	1	1	1	1	0.75
c_2	0.85252	0.91771	0.85252	0.85252	0.91771	0.84665	0.92171
c_3	0	1	0	0	1	0	1
c_4	3	1	4	2	1	4	1
c_5	0	1	0	0	1	0	1
$C_{1\sigma}$	0.5	0.75	0.5	0.5	0.75	0.5	0.75
$C_{2\sigma}$	0.85252	1	0.85252	1	1	0.85252	1
V_s (eV)	-101.12679	-37.10024	-104.37986	-32.93291	-39.09538	-104.73877	-39.48897
V_p (eV)	20.69825	13.17125	20.85777	10.10210	13.45505	20.90891	14.45367
T (eV)	34.31559	11.58941	35.96751	9.07768	12.74462	36.26840	15.86820
V_{ss} (eV)	-17.15779	-5.79470	-17.98376	-4.53884	-6.37231	-18.13420	-7.93410
$E(sp\ no)$ (eV)	0	-14.63489	0	-14.63489	-14.63489	0	-14.53414
$\Delta E_{H_2MO}(sp\ no)$ (eV)	0	-1.13379	-2.26759	-1.29147	-2.26758	-2.42526	0
$E_T(sp\ no)$ (eV)	0	-13.50110	2.26759	-13.34342	-12.36731	2.42526	-14.53414
$E_T(H_2MO)$ (eV)	-63.27075	-31.63539	-63.27075	-31.63539	-31.63533	-63.27040	-31.63534
$E_T(atom-atom,msp^3.AO)$ (eV)	-2.26759	-0.56690	-2.26759	-1.29147	0	-2.42526	0
$E_T(sp)$ (eV)	-65.53833	-32.20226	-65.53833	-32.92684	-31.63537	-65.69600	-31.63537
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	15.4421	21.8249	28.9084	54.5632	48.7771
E_K (eV)	32.73133	17.43132	10.16428	14.36554	19.02803	35.91442	32.10594
$\overline{E}_{ps}$ (eV)	-0.35806	-0.26130	-0.20668	-0.24690	-0.27301	-0.38945	-0.35462
$\overline{E}_{Kish}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.17897 [6]	0.12312 [2]	0.39427 [56]	0.11159 [12]	0.40696 [24]
$\overline{E}_{exc}$ (eV)	-0.25982	-0.08364	-0.11720	-0.18534	-0.07587	-0.33365	-0.15115
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(group)$ (eV)	-49.54347	-32.28590	-65.77272	-33.11218	-31.71124	-66.36330	-31.78651
$E_{united}(c_1\ no\ no)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414
$E_{united}(c_2\ no\ no)$ (eV)	0	-13.59844	0	0	-13.59844	0	-13.59844
$E_{ps}(group)$ (eV)	5.63881	3.90454	7.23317	3.84240	3.32988	7.82374	3.51208

Table 15.325. The total bond energies of indole calculated using the functional group composition and the energies of Table 15.324 compared to the experimental values [2].

Formula	Name	$C=C$	CH (i)	$C=C$	$C-C$	CH (ii)	$C-N-C$	NH	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C_8H_7N	Indole	6	4	1	1	2	1	1	78.52215	78.514	-0.00010

Table 15.326. The bond angle parameters of indole and experimental values [1]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T\left(atom-atom,msp^3.AO\right)$.

Atoms of Angle	$2c'$ Bond 1 (a_0)	$2c'$ Bond 2 (a_0)	$2c'$ Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle CCC$ (aromatic)	2.62936	2.62936	4.5585	-17.17218	20	-17.17218	20	0.79232	0.79232	1	1	1	0.79232	-1.85836				120.19	120 [50-52] (benzene)
$\angle CCH$ (aromatic)																120.19		119.91	120 [50-52] (benzene)

ADENINE

Adenine having the formula $C_5H_5N_5$ comprises a pyrimidine moiety with an aniline group and a conjugated five-membered ring which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 75. The aromatic $C\overset{3e}{=}C$, $C-H$, and $C\overset{3e}{=}N$ functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The NH_2 and C_a-N_a functional groups of the aniline moiety are equivalent to those of aniline as given in the corresponding section. The CH, NH, C_d-N_e, and $N_e=C_e$ groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The $C-N-C$ functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the $C-N-C$ group bonding to aryl and alkenyl groups.

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.332 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.79-15.108) are given in Table 15.332.

Table 15.327. The symbols of functional groups of adenine.

Functional Group	Group Symbol
CC (aromatic bond)	$C\overset{3e}{=}C$
CH (aromatic)	CH (i)
$C_{b,c}\overset{3e}{=}N_c$ $C_{a,b}\overset{3e}{=}N_b$	$C\overset{3e}{=}N$
C_a-N_a	$C-N$ (a)
NH_2 group	NH_2
$N_e=C_e$ double bond	$N=C$
C_d-N_e	$C-N$ (b)
N_dH group	NH
CH	CH (ii)
$C_c-N_d-C_e$	$C-N-C$

Table 15.328. The geometrical bond parameters of adenine and experimental values [1].

Parameter	$C \overset{3e}{=} C$ Group	CH (i) Group	$C \overset{3e}{=} N$ Group	$C-N$ (a) Group	NH_2 Group	$N=C$ Group	$C-N$ (b) Group	NH Group	CH (ii) Group	$C-N-C$ Group
$a\ (a_0)$	1.47348	1.60061	1.47169	1.81158	1.24428	1.44926	1.82450	1.24428	1.53380	1.44394
$c^1\ (a_0)$	1.31468	1.03299	1.27073	1.34595	0.94134	1.30383	1.35074	0.94134	1.01120	1.30144
Bond Length $2c^1\ (A)$	1.39140	1.09327	1.34489	1.42449	0.99627	1.37991	1.42956	0.996270	1.07021	1.37738
Exp. Bond Length (A)	1.393 (pyrimidine)	1.084 (pyridine)	1.340 (pyrimidine)	1.431 (aniline)	0.998 (aniline)			0.996 (pyrrole)	1.076 (pyrrole)	1.370 (pyrrole)
$b, c\ (a_0)$	0.66540	1.22265	0.74237	1.21254	0.81370	0.63276	1.22650	0.81370	1.15326	0.62548
e	0.89223	0.64537	0.86345	0.74297	0.75653	0.89965	0.74033	0.75653	0.65928	0.90131

Table 15.329. The MO to HO intercept geometrical bond parameters of adenine. R_i is an alkyl group and R, R', R'' are H or alkyl groups. E_T is $E_T\left(atom-atom, msp^3.AO\right)$.

Bond	Atom	E_T (eV) Bond 1	E_T (eV) Bond 2	E_T (eV) Bond 3	E_T (eV) Bond 4	Final Total Energy $C2sp^3$ (eV)	$r_{initial}$ (a_0)	r_{final} (a_0)	$E_{Covalent}(C2sp^3)$ (eV) Final	$E(C2sp^3)$ (eV) Final	θ^* $(^\circ)$	θ_1 $(^\circ)$	θ_2 $(^\circ)$	d_1 (a_0)	d_2 (a_0)
$C_d(N_b)C_nN_nH-H$	N_n	-0.56690	0	0	0		0.93084	0.88392	-15.39265		121.74	58.26	67.49	0.47634	0.46500
$C_d(N_b)C_n-N_nH_2$	C_n	-0.56690	-0.54343	-0.85035	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	89.90	90.10	41.95	1.34737	0.00142
$C_d(N_b)C_n-N_nH_2$	N_n	-0.56690	0	0	0		0.93084	0.88392	-15.39265		96.32	83.68	46.43	1.24859	0.09736
$C-H\ (C_bH)$	C_b	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28864	78.27	101.73	41.39	1.20084	0.16785
$C-H\ (C_eH)$	C_e	-0.92918	-0.60631	0	0	-153.15119	0.91771	0.83159	-16.36125	-16.17038	79.01	100.99	41.89	1.19159	0.15860
$N-H\ (N_dH)$	N	-0.60631	-0.60631	0	0		0.93084	0.84833	-16.03838		119.52	60.48	65.13	0.52338	0.41796
$C_d(NH_2)C_n \overset{3e}{=} N_bC_b$	C_n	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	128.54	51.46	58.65	0.76572	0.50501
$C_d(NH_2)C_n \overset{3e}{=} N_bC_b$ $N_bC_b \overset{3e}{=} N_eC_e$	N_b N_e	-0.54343	-0.54343	0	0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	0.55656
$N_bC_b \overset{3e}{=} N_eC_e$ $C_nN_b \overset{3e}{=} C_bN_e$	C_b	-0.54343	-0.54343	-0.56690	0	-153.26945	0.91771	0.82562	-16.47951	-16.28865	129.26	50.74	59.44	0.74824	0.52249
$C_d(N_dH)C_e \overset{3e}{=} N_eC_b$	C_e	-0.85035	-0.54343	-0.60631	0	-153.61578	0.91771	0.80863	-16.82584	-16.63498	128.45	51.55	58.55	0.76792	0.50281
$N_b(N_nH_2)C_n \overset{3e}{=} C_d(N_e)C_e$	C_n	-0.85035	-0.54343	-0.56690	0	-153.57636	0.91771	0.81052	-16.78642	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$N_b(N_nH_2)C_n \overset{3e}{=} C_d(N_e)C_e$ $C_n(N_e)C_d \overset{3e}{=} C_e(N_dH)N_e$	C_d	-0.85035	-0.85035	-0.46459	0	-153.78097	0.91771	0.80076	-16.99103	-16.80017	134.44	45.56	59.22	0.75398	0.56071
$C_n(N_e)C_d \overset{3e}{=} C_e(N_dH)N_e$	C_e	-0.85035	-0.54343	-0.60631	0	-153.61578	0.91771	0.80863	-16.82584	-16.63498	134.77	45.23	59.62	0.74516	0.56952
$C_d(N_e)C_e-N_dH$	C_e	-0.85035	-0.54343	-0.60631	0	-153.61578	0.91771	0.80863	-16.82584	-16.63498	137.54	42.46	60.78	0.70488	0.59656
$C_e(H)N_d-C_e(N_e)C_d$ $N_e(H)C_e-N_d(H)C_e$	N_d	-0.60631	-0.60631	0	0		0.93084	0.84833	-16.03838		139.04	40.96	62.76	0.66083	0.64061
$N_e(H)C_e-N_d(H)C_e$	C_e	-0.60631	-0.92918	0	0	-153.15119	0.91771	0.83159	-16.36125	-16.17039	138.42	41.58	61.93	0.67940	0.62203
$C_dN_e=C_e(H)N_dH$	C_e	-0.92918	-0.60631	0	0	-153.15119	0.91771	0.83159	-16.36125	-16.17039	137.93	42.07	61.72	0.68657	0.61726
$C_dN_e=C_e(H)N_dH$	N_e	-0.92918	-0.46459	0	0		0.93084	0.83885	-16.21952		138.20	41.80	62.08	0.67849	0.62534
$C_d(C_e)C_d-N_eC_e$	N_e	-0.46459	-0.92918	0	0		0.93084	0.83885	-16.21952		91.32	88.68	43.14	1.33135	0.01939
$C_d(C_e)C_d-N_eC_e$	C_d	-0.46459	-0.85035	-0.85035	0	-153.78097	0.91771	0.80076	-16.99103	-16.80017	87.71	92.29	40.72	1.38280	0.03206

Table 15.330. The energy parameters (eV) of functional groups of adenine.

Parameters	$C\overset{3e}{=}C$ Group	CH (i) Group	$C\overset{3e}{=}N$ Group	$C-N$ (a) Group	NH_2 Group	$N=C$ Group	$C-N$ (b) Group	NH Group	CH (ii) Group	$C-N-C$ Group
f_1	0.75	1	0.75	1	1	1	1	1	1	1
n_1	2	1	2	1	2	2	1	1	1	2
n_2	0	0	0	0	0	0	0	0	0	0
n_3	0	0	0	0	1	0	0	0	0	0
C_1^*	0.5	0.75	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.5
C_2^*	0.85252	1	0.91140	1	0.93613	0.85252	1	0.93613	1	0.85252
c_1	1	1	1	1	0.75	1	1	0.75	1	1
c_2	0.85252	0.91771	0.91140	0.84665	0.92171	0.84665	0.84665	0.92171	0.91771	0.84665
c_3	0	1	0	0	0	0	0	1	1	0
c_4	3	1	3	2	1	4	2	1	1	4
c_5	0	1	0	0	2	0	0	1	1	0
C_{1o}^*	0.5	0.75	0.5	0.5	1.5	0.5	0.5	0.75	0.75	0.5
C_{2o}^*	0.85252	1	0.91140	1	1	0.85252	1	1	1	0.85252
$V_e\ (eV)$	-101.12679	-37.10024	-102.01431	-32.76465	-78.97795	-103.92756	-32.44864	-39.48897	-39.09538	-104.73877
$V_p\ (eV)$	20.69825	13.17125	21.41410	10.10870	28.90735	20.87050	10.07285	14.45367	13.45505	20.90891
$T\ (eV)$	34.31559	11.58941	34.65890	9.04312	31.73641	35.85539	8.89248	15.86820	12.74462	36.26840
$V_{ne}\ (eV)$	-17.15779	-5.79470	-17.32945	-4.52156	-15.86820	-17.92770	-4.44624	-7.93410	-6.37231	-18.13420
$E(no\ no)\ (eV)$	0	-14.63489	0	-14.63489	-14.53414	0	-14.63489	-14.53414	-14.63489	0
$\Delta E_{no,no}(no\ no)\ (eV)$	0	-1.13379	0	-1.13379	0	-1.85836	-0.92918	0	-2.26758	-2.42526
$E_T(no\ no)\ (eV)$	0	-13.50110	0	-13.50110	-14.53414	1.85836	-13.70571	-14.53414	-12.36731	2.42526
$E(n_o\ no\ no)\ (eV)$	0	0	0	0	-14.53414	0	0	0	0	0
$E_T(n_o no)\ (eV)$	-63.27075	-31.63539	-63.27076	-31.63549	-48.73654	-63.27100	-31.63527	-31.63534	-31.63533	-63.27040
$E_T\left(atom-atom,msp^3.AO\right)\ (eV)$	-2.26759	-0.56690	-1.44915	-1.13379	0	-1.85836	-0.92918	0	0	-2.42526
$E_T(no)\ (eV)$	-65.53833	-32.20226	-64.71988	-32.76916	-48.73660	-65.12910	-32.56455	-31.63537	-31.63537	-65.69600
$\omega\left(10^{15}\ rad/s\right)$	49.7272	26.4826	43.6311	11.9890	68.9812	15.4704	21.5213	48.7771	28.9084	54.5632
$E_K\ (eV)$	32.73133	17.43132	28.71875	7.89138	45.40465	10.18290	14.16571	32.10594	19.02803	35.91442
$\bar{E}_D\ (eV)$	-0.35806	-0.26130	-0.33540	-0.18211	-0.42172	-0.20558	-0.24248	-0.35462	-0.27301	-0.38945
$\bar{E}_{Resb}\ (eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]	0.15498 [54]	0.40929 [22]	0.20768 [58]	0.12944 [23]	0.40696 [24]	0.39427 [56]	0.11159 [12]
$\bar{E}_{exc}\ (eV)$	-0.25982	-0.08364	-0.23715	-0.10462	-0.21708	-0.10174	-0.17775	-0.15115	-0.07587	-0.33365
$E_{ang}\ (eV)$	0.14803	0.14803	0.09457	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(Group)\ (eV)$	-49.54347	-32.28590	-48.82472	-32.87379	-49.17075	-65.33259	-32.74230	-31.78651	-31.71124	-66.36330
$E_{mutual}(e_s\ no\ no)\ (eV)$	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
$E_{mutual}(e_s\ no\ no)\ (eV)$	0	-13.59844	0	0	-13.59844	0	0	-13.59844	-13.59844	0
$E_D(Group)\ (eV)$	5.63881	3.90454	4.92005	3.60401	7.43973	6.79303	3.47253	3.51208	3.32988	7.82374

Table 15.331. The total bond energies of adenine calculated using the functional group composition and the energies of Table 15.330 compared to the experimental values [2].

Formula	Name	$C\overset{3e}{=}C$	CH (i)	$C\overset{3e}{=}N$ Group	$C-N$ (a) Group	NH_2 Group	$N=C$	$C-N$ (b)	NH	CH (ii)	$C-N-C$	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_5N_5$	Adenine	2	1	4	1	1	1	1	1	1	1	70.83735	70.79811	-0.00055

Table 15.332. The bond angle parameters of adenine and experimental values [61]. In the calculation of θ_v, the parameters from the preceding angle were used. E_T is $E_T(atom-atom, msp^3.AO)$.

Atoms of Angle	2c' Bond 1 (a_0)	2c' Bond 2 (a_0)	2c' Terminal Atoms (a_0)	$E_{Coulombic}$ Atom 1	Atom 1 Hybridization Designation (Table 15.3B)	$E_{Coulombic}$ Atom 2	Atom 2 Hybridization Designation (Table 15.3B)	c_2 Atom 1	c_2 Atom 2	C_1	C_2	c_1	c_2'	E_T (eV)	θ_v (°)	θ_1 (°)	θ_2 (°)	Cal. θ (°)	Exp. θ (°)
$\angle HNH$	1.88268	1.88268	3.1559	-14.53414	N	H	H	0.93613 Eq. (13.248))	1	1	1	0.75	1.06823	0				113.89	113.9 [1] (aniline)
$\angle HNC_a$	1.88268	2.69190	4.0497	-14.53414	N	-15.95955	6	0.84665 (Eq. (15.152))	0.86284 (Eq. (15.64))	0.75	1	0.75	1.01912	0				123.60	118
$\angle H_bC_bN_b$ $\angle H_bC_bN_c$	2.06598	2.54147	3.9497	-14.82575	1	-14.53414	N	0.91771	0.91140 Eq. (15.116))	0.75	1	0.75	0.99312	0				117.65	115 116
$\angle H_cC_cN_c$	2.02241	2.60766	4.0661	-16.36125	10	-14.53414	N	0.83159	0.84665 Eq. (15.152))	0.75	1	0.75	1.01811	0				122.35	126
$\angle H_cC_cN_d$																122.35	112.64	125.02	119
$\angle H_dN_dC_c$ $\angle H_dN_dC_c$	1.88268	2.60287	4.0497	-14.53414	N	-15.95955	6	0.84665 (Eq. (15.152))	0.86284 (Eq. (15.64))	0.75	1	0.75	1.10912	0				128.35	127
$\angle N_cC_cN_d$	2.60766	2.60287	4.3359	-16.21952	8	-16.03838	7	0.83885	0.84833	1	1	1	0.84359	-1.44915				112.64	114.4
$\angle N_cC_cN_d$	2.54147	2.60287	4.6260	-14.53414	N	-14.53414	N	0.91140 Eq. (15.116))	0.84665 Eq. (15.152))	1	1	1	0.87902	-1.44915				128.11	127.8
$\angle N_bC_bN_c$	2.54147	2.54147	4.5826	-15.55033	3	-15.55033	3	0.87495	0.87495	1	1	1	0.87495	-1.44915				128.73	128.9
$\angle N_bC_aN_a$	2.54147	2.69190	4.5826	-15.91261	5	-15.39265	2	0.85503	0.88392	1	1	1	0.86947	-1.44915				122.22	119.7
$\angle N_cC_dC_c$	2.70148	2.62936	4.3818	-14.53414	N	-15.95955 C_c	6	0.84665 (Eq. (15.152))	0.85252	1	1	1	0.84958	-1.44915				110.56	110.4
$\angle N_dC_cC_d$	2.60287	2.62936	4.1952	-14.53414	N	-16.99103 C_d	16	0.84665 (Eq. (15.152))	0.80076	1	1	1	0.82371	-1.44915				106.60	105.9
$\angle N_cC_cC_d$	2.54147	2.62936	4.4721	-14.53414	N	-16.99103 C_d	16	0.91140 Eq. (15.116))	0.80076	1	1	1	0.85608	-1.44915				119.73	126.4
$\angle N_bC_aC_d$	2.54147	2.62936	4.4721	-14.53414	N	-16.99103 C_d	16	0.91140 Eq. (15.116))	0.80076	1	1	1	0.85608	-1.44915				119.73	118.2
$\angle N_aC_aC_a$	2.69190	2.62936	4.5607	-14.53414	N	-16.52644 C_d	12	0.91140 Eq. (15.116))	0.82327	1	1	1	0.86734	-1.44915				117.97	122.1
$\angle N_cC_aC_a$	2.70148	2.62936	4.8990	-14.53414	N	-14.82575 C_a	1	0.91140 Eq. (15.116))	0.91771	1	1	1	0.91456	-1.44915				133.55	132.8
$\angle C_dN_cC_c$	2.70148	2.60766	4.2661	-17.92022	28	-17.92022	28	0.75924	0.75924	1	1	1	0.75924	-1.85836				106.93	103.3
$\angle C_cN_dC_c$	2.60287	2.60287	4.2661	-17.75502	25	-17.75502	25	0.76631	0.76631	1	1	1	0.76631	-1.85836				110.07	106.1
$\angle C_bN_cC_c$	2.54147	2.54147	4.3589	-17.40869	21	-17.75502	25	0.78155	0.76631	1	1	1	0.77393	-1.85836				118.09	111.3
$\angle C_aN_bC_b$	2.54147	2.54147	4.3704	-17.71560	24	-17.40869	21	0.76801	0.78155	1	1	1	0.77478	-1.85836				118.59	118.6
$\angle C_aC_aC_c$	2.62936	2.62936	4.4721	-17.71560	24	-17.14871	19	0.76801	0.79340	1	1	1	0.78071	-1.85836				116.52	116.7

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

I CLAIM:

1. A system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising:

processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and

an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

2. The system of claim 1 wherein the output device is a display that displays at least one of visual or graphical media.

3. The system of claim 2 wherein the display is at least one of static or dynamic.

4. The system of claim 3 wherein at least one of vibration and rotation is be displayed.

5. The system of claim 4 wherein displayed information is used to model reactivity and physical properties.

6. The system of claim 5, wherein the output device is a monitor, video projector, printer, or three-dimensional rendering device.

7. The system of claim 6 wherein displayed information is used to model other species and provides utility to anticipate their reactivity and physical properties.

8. The system of claim 7 wherein the processing means is a general purpose computer.

9. The system of claim 8 wherein the general purpose computer comprises a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input means.

10. The system of claim 9, wherein the input means comprises a serial port, usb port, microphone input, camera input, keyboard or mouse.

11. The system of claim 10 wherein the processing means comprises a special purpose computer or other hardware system.

12. The system of claim 11 further comprising computer program products.

13. The system of claim 12 further comprising computer readable medium having embodied therein program code means.

14. The system of claim 13 wherein the computer readable media is any available media which can be accessed by a general purpose or special purpose computer.

15. The system of claim 14 wherein the computer readable media comprises at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium which can embody the desired program code means and which can be accessed by a general purpose or special purpose computer.

16. The system of claim 15 wherein the program code means comprises executable instructions and data which cause a general purpose computer or special purpose computer to perform a certain function of a group of functions.

17. The system of claim 16 wherein the program code is Mathematica programmed with an algorithm based on the physical solutions, and the computer is a PC.

18. The system of claim 17 wherein the algorithm is ParametricPlot3D[{2*Sqrt[1-z*z]*Cos[u],Sqrt[(1-z*z)]*Sin[u],z},{u,0,2* Pi},{z,-1,.9999}], and the rendering is viewed from different perspectives.

19. The system of claim 18 wherein the algorithms for viewing from different perspectives comprises Show[Out[1], ViewPoint->{x,y,z}] where x, y, and z are Cartesian coordinates.

20. The system of claim 19 wherein the physical, Maxwellian solutions of the charge, mass, and current density functions of said specie comprises a solution of the classical wave equation $\left[\nabla^2 - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right]\rho(r,\theta,\phi,t) = 0$ which is the equation of motion of the charge.

21. The system of claim 20 wherein the boundary constraint of the wave equation solution is nonradiation according to Maxwell's equations.

22. The system of claim 21 wherein the boundary condition is met for an ellipsoidal-time harmonic function when

$$\omega_n = \frac{\pi\hbar}{m_e A} = \frac{\hbar}{m_e ab}$$

where the area of an ellipse is

$$A = \pi ab$$

where $2b$ is the length of the semiminor axis and $2a$ is the length of the semimajor axis.

23. The system of claim 22 wherein the specie charge and current density functions, bond distance, and energies are solved from the Laplacian in ellipsoidal coordinates:

$$(\eta-\zeta)R_\xi\frac{\partial}{\partial\xi}(R_\xi\frac{\partial\phi}{\partial\xi}) + (\zeta-\xi)R_\eta\frac{\partial}{\partial\eta}(R_\eta\frac{\partial\phi}{\partial\eta}) + (\xi-\eta)R_\zeta\frac{\partial}{\partial\zeta}(R_\zeta\frac{\partial\phi}{\partial\zeta}) = 0 .$$

with the constraint of nonradiation.

24. The system of claim 23 wherein each bond of the said specie defined as a molecular orbital (MO) has the ellipsoidal charge-density function given by

$$\sigma = \frac{q}{4\pi abc}\frac{1}{\sqrt{\frac{x^2}{a^4}+\frac{y^2}{b^4}+\frac{z^2}{c^4}}}$$

25. The system of claim 24 wherein the bonds of the said specie defined as a molecular orbital (MO) has the charge-density function comprising a linear combination of ellipsoids wherein the charge density of one said ellipsoid is given by

$$\sigma = \frac{q}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^4} + \frac{y^2}{b^4} + \frac{z^2}{c^4}}}$$

26. The system of claim 25 wherein the equation of motion has the parametric form

$$r(t) = \mathbf{i}a\cos\omega t + \mathbf{j}b\sin\omega t$$

27. The system of claim 26 wherein he force balance of the hydrogen-type molecular ion ellipsoidal MO is given by

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\varepsilon_0} D$$

$$a = 2a_0$$

28. The system of claim 27 where the force constant k of a H_2^+-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k = \frac{2e^2}{4\pi\varepsilon_o}$$

29. The system of claim 28 wherein the distance from the origin of the H_2-type-ellipsoidal-MO to each focus c' is given by :

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{aa_0}{2}}$$

30. The system of claim 29 wherein the internuclear distance $2c'$ is given by:

$$2c' = 2\sqrt{\frac{aa_0}{2}}$$

31. The system of claim 30 wherein the length of the semiminor axis of the prolate spheroidal H_2-type MO $b = c$ is given by:

$$b = \sqrt{a^2 - c'^2}$$

32. The system of claim 31 wherein the length of the semiminor axis of the prolate spheroidal H_2-type MO $b = c$ is given by:

$$e = \frac{c'}{a}$$

33. The system of claim 32 wherein the internuclear distance, $2c'$, which is the distance between the foci is

$$2c' = 2a_o;$$

the semiminor axis is

$$b = \sqrt{3}a_o, \text{ and}$$

the eccentricity, e, is

$$e = \frac{1}{2}.$$

34. The system of claim 33 wherein the potential energy of the electron in the central field of the protons at the foci is

$$V_e = \frac{-4e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}$$
$$= \frac{-4e^2}{8\pi\varepsilon_o c'}\ln\frac{a+c'}{a-c'} \quad ;$$
$$= \frac{-4e^2}{8\pi\varepsilon_o a_H}\ln 3 = -59.7575\ eV$$

The potential energy of the two protons is

$$V_p = \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} = \frac{e^2}{8\pi\varepsilon_o a_H} = 13.5984\ eV;$$

The kinetic energy of the electron is

$$T = \frac{2\hbar^2}{m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \frac{2e^2}{8\pi\varepsilon_o a_H}\ln 3 = 29.8787\ eV, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms:

$$E_T = V_e + T + V_p$$

$$E_T = \frac{-e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[\left(4-\frac{4}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]$$
$$= \frac{-e^2}{8\pi e_o a_H}(4\ln 3-1-2\ln 3)$$
$$= -16.2803\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

35. The system of claim 34 wherein during bond formation, the electron undergoes a reentrant oscillatory orbit with vibration of the protons, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{\frac{e^2}{8\pi\varepsilon_o a_H}(4\ln 3-1-2\ln 3)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{2e^2}{4\pi\varepsilon_o\left(2a_H\right)^3}}{m_e}}{m_e c^2}}\right]-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$
$$= -16.2803\ eV - 0.118811\ eV + \frac{1}{2}(0.29282\ eV)$$
$$= -16.2527\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

36. The system of claim 35 wherein the bond dissociation energy, E_D, is the difference between the total energy of the hydrogen atom and E_T:

$$E_D = E(H) - E_T = 2.654\ eV$$

wherein the total energy of a hydrogen atom is $E(H) = -13.59844\ eV$, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

37. The system of claim 36 wherein the H_2^+-type ellipsoidal MO and the hydrogen atomic orbital (AO) serve as basis functions for the MOs of specie.

38. The system of claim 37 wherein the MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of $\hbar$.

39. The system of claim 38 wherein the potential energy of electron in the central field of the protons at the foci is

$$V_e = \frac{-4e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \frac{-4e^2}{8\pi\varepsilon_o c'}\ln\frac{a+c'}{a-c'};$$

The potential energy of the two protons is

$$V_p = \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} = \frac{e^2}{8\pi\varepsilon_0 c'};$$

The kinetic energy of the electron is

$$T = \frac{2\hbar^2}{m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = \frac{2\hbar^2}{m_e a c'}\ln\frac{a+c'}{a-c'}, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms:

$$E_T = V_e + T + V_p$$

$$E_T = \frac{-e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[\left(4-\frac{4}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right] = \frac{-e^2}{8\pi\varepsilon_o c'}\left[\left(4-\frac{4}{a}\right)\ln\frac{a+c'}{a-c'}-1\right].$$

40. The system of claim 39 wherein during bond formation, the electron undergoes a reentrant oscillatory orbit with vibration of the protons, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{ \frac{-e^2}{8\pi\varepsilon_o c'}\left[\left(4-\frac{4}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{2e^2}{4\pi\varepsilon_o (a)^3}}{m_e}}{m_e c^2}}\right]-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

41. The system of claim 40 wherein the force balance equation derived of a H_2-type ellipsoidal MO is given by

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{pe^2}{8\pi\varepsilon_o a b^2} D + \frac{\hbar^2}{2 m_e a^2 b^2} D$$

$$a = \frac{a_0}{p}$$

42. The system of claim 41 where the force constant k of a H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k = \frac{2e^2}{4\pi\varepsilon_o}$$

43. The system of claim 42 wherein the distance from the origin of the H_2-type-ellipsoidal-MO to each focus c' is given by :

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2a}} = \sqrt{\frac{a a_0}{2}}$$

44. The system of claim 43 wherein the internuclear distance $2c'$ is given by:

$$2c' = 2\sqrt{\frac{a a_0}{2}}$$

45. The system of claim 44 wherein the length of the semiminor axis of the prolate spheroidal H_2-type MO $b = c$ is given by:

$$b = \sqrt{a^2 - c'^2}$$

46. The system of claim 45 wherein the length of the semiminor axis of the prolate spheroidal H_2-type MO $b = c$ is given by:

$$e = \frac{c'}{a}$$

47. The system of claim 46 wherein the internuclear distance, $2c'$, which is the distance between the foci is

$$2c' = \sqrt{2}a_o;$$

the semiminor axis is

$b = \frac{1}{\sqrt{2}} a_o$, and

the eccentricity, e, is

$$e = \frac{1}{\sqrt{2}}.$$

48. The system of claim 47 wherein the potential energy of the two electrons in the central field of the protons at the foci is

$$V_e = \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -67.8358\ eV;$$

The potential energy of the two protons is

$$V_p = \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} = 19.2415\ eV;$$

The kinetic energy of the electrons is

$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 33.9179\ eV$, and

The energy, V_m, of the magnetic force between the electrons is

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = -16.9589\ eV, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$E_T = -13.60\ eV\left[\left(2p^2\sqrt{2} - p^2\sqrt{2} + \frac{p^2\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - p^2\sqrt{2}\right] = -p^2 31.63$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

49. The system of claim 48 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the protons, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{\frac{e^2}{8\pi\varepsilon_o a_0}\left[\left(2\sqrt{2} - \sqrt{2} + \frac{\sqrt{2}}{2}\right)\ln\frac{\sqrt{2}+1}{\sqrt{2}-1} - \sqrt{2}\right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o a_0^3}}}{m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

$$= -31.635\ eV - 0.326469\ eV + \frac{1}{2}(0.56764\ eV)$$

$$= -31.6776\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

50. The system of claim 49 wherein the bond dissociation energy, E_D, is the difference between the total energy of the hydrogen atoms and E_T:

$$E_D = E(2H[a_H]) - E_T = 4.478\ eV$$

wherein the total energy of two hydrogen atoms is $E(2H[a_H]) = -27.21\ eV$, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

51. The system of claim 50 wherein the H_2-type ellipsoidal MO and the hydrogen atomic orbital (AO) serve as basis functions for the MOs of the specie.

52. The system of claim 51 wherein the MO must (1) be a solution of Laplace's equation to give a equipotential energy surface, (2) correspond to an orbital solution of the Newtonian equation of motion in an inverse-radius-squared central field having a constant total energy, (3) be stable to radiation, and (4) conserve the electron angular momentum of $\hbar$.

53. The system of claim 52 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}};$$

The potential energy of the two nuclei is

$$V_p = \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}};$$

The kinetic energy of the electrons is

$$T = \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The energy, V_m, of the magnetic force between the electrons is

$$V_m = \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$E_T = -\frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right] = -\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right].$$

54. The system of claim 53 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

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$$E_T = -\left\{\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right]-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

55. The system of claim 54 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{\frac{e^2}{8\pi\varepsilon_0 c'}\left[\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{e^2}{4\pi\varepsilon_o b^3}}}{m_e c^2}}\right]-\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

56. The system of claim 55 wherein the energy of the MO is matched to that of the outermost atomic orbital of a bonding heteroatom in the case where a minimum energy is achieved with a direct bond to the AO.

57. The system of claim 56 wherein the MO is continuous with the AO containing paired electrons that do not participate in the bond, and said paired electrons provide a means for the energy matched MO to form a continuous equipotential energy surface.

58. The system of claim 57 wherein an independent MO is formed such that the AO force balance causes the remaining electrons to be at lower energy and a smaller radius.

59. The system of claim 58 wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum.

60. The system of claim 59 wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum.

61. The system of claim 60 wherein at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals.

62. The system of claim 61 where the force constant k' of a H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{c_1 c_2 2e^2}{4\pi\varepsilon_o}$$

where c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond.

63. The system of claim 62 where the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2k' a}} = \sqrt{\frac{aa_0}{2k'}};$$

the internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2k'}};$$

the length of the semiminor axis of the prolate spheroidal MO $b = c$ is given by

$b = \sqrt{a^2 - c'^2}$, and

and, the eccentricity, e, is

$$e = \frac{c'}{a}.$$

64. The system of claim 63 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}};$$

The potential energy of the two nuclei is

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}};$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The energy, V_m, of the magnetic force between the electrons is

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$E_T = -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]$$
$$= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

65. The system of claim 64 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_1 c_2 e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right]-n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

66. The system of claim 65 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_1 c_2 e^2}{4\pi\varepsilon_o b^3}}}{m_e c^2}}\right]-n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

67. The system of claim 66 wherein a hybridized shell comprises a linear combination of the electrons of at least two atomic-orbital shells.

68. The system of claim 67 wherein the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for

each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons.

69. The system of claim 68 wherein the total energy $E_T\left(atom, msp^3\right)$ (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least two AO shells

70. The system of claim 69 wherein the radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{(Z-q)e^2}{8\pi\varepsilon_0 E_T\left(atom, msp^3\right)}$$

71. The system of claim 70 wherein the Coulombic energy $E_{Coulomb}\left(atom, msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by

$$E_{Coulomb}\left(atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}$$

72. The system of claim 71 wherein the during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO) and the energy change the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r_n of the AO electron:

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_n\right)^3} = \frac{8\pi\mu_o\mu_B^2}{\left(r_n\right)^3}$$

73. The system of claim 72 wherein the energy $E\left(atom, msp^3\right)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}\left(atom, msp^3\right)$ and $E(magnetic)$:

$$E\left(atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_n\right)^3}$$

74. The system of claim 73 wherein at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals; the total energy of the hybridized orbitals is given by the sum of $E\left(atom, msp^3\right)$ and the next energies of successive ions of the atom over the n electrons comprising total electrons of the at least two initial AO shells; is the sum of the first energy of the atom and the hybridization energy.

75. The system of claim 74 wherein the sharing of electrons between two *atom* msp^3 HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy.

76. The system of claim 75 wherein in order to further satisfy the potential, kinetic, and orbital energy relationships, each *atom* msp^3 HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond.

77. The system of claim 76 wherein the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons and the hybridization energy.

78. The system of claim 77 wherein the total energy $E_T\left(mol.atom, msp^3\right)$ (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least two initial AO shells and the hybridization energy.

79. The system of claim 78 wherein the radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3} = \left(\sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25) \right) \frac{e^2}{8\pi\varepsilon_0 E_T\left(mol.atom, msp^3\right)}$$

where $s = 1,2,3$ for a single, double, and triple bond, respectively.

80. The system of claim 79 wherein the Coulombic energy $E_{Coulomb}\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by

$$E_{Coulomb}\left(mol.atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}$$

81. The system of claim 80 wherein the during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO) and the energy change the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r_n of the AO electron:

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_n\right)^3} = \frac{8\pi\mu_o\mu_B^2}{\left(r_n\right)^3}$$

82. The system of claim 81 wherein the energy $E\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom, msp^3\right)$ and $E(magnetic)$:

$$E\left(mol.atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_n\right)^3}$$

83. The system of claim 82 wherein $E_T\left(atom - atom, msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between $E\left(mol.atom, msp^3\right)$ and $E\left(atom, msp^3\right)$.

$$E_T\left(atom - atom, msp^3\right) = E\left(mol.atom, msp^3\right) - E\left(atom, msp^3\right)$$

84. The system of claim 83 wherein to meet an energy matching condition for all MOs at all HOs, the energy $E\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell of each bonding atom must be the average of $E\left(mol.atom, msp^3\right)$ for two different values of s:

$$E\left(mol., msp^3\right) = \frac{E\left(mol(s_1), msp^3\right) + E\left(mol(s_2), msp^3\right)}{2} \qquad (14.512)$$

85. The system of claim 84 wherein $E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO, is average of $E_T\left(atom-atom,msp^3\right)$ for two different values of s:

$$E_T\left(atom-atom,msp^3\right)=\frac{E_T\left(atom-atom(s_1),msp^3\right)+E_T\left(atom-atom(s_2),msp^3\right)}{2}$$

86. The system of claim 85 wherein the radius r_{msp^3} of the *atom* msp^3 shell of each bonding atom is given by the Coulombic energy using the initial energy $E_{Coulomb}\left(atom,msp^3\right)$ and $E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO:

$$r_{msp^3}=\frac{-e^2}{8\pi\varepsilon_0 a_0\left(E_{Coulomb}\left(atom,msp^3\right)+E_T\left(atom-atom,msp^3\right)\right)} \qquad (14.514)$$

87. The system of claim 86 wherein the Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by

$$E_{Coulomb}\left(mol.atom,msp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}}$$

88. The system of claim 87 wherein the during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO) and the energy change the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r_n of the AO electron:

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_n\right)^3}=\frac{8\pi\mu_o\mu_B^2}{\left(r_n\right)^3}.$$

89. The system of claim 88 wherein the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of

the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom, msp^3\right)$ and $E(magnetic)$:

$$E\left(mol.atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_n\right)^3}$$

90. The system of claim 89 wherein $E_T\left(atom-atom, msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between $E\left(mol.atom, msp^3\right)$ and $E\left(atom, msp^3\right)$.

$$E_T\left(atom-atom, msp^3\right) = E\left(mol.atom, msp^3\right) - E\left(atom, msp^3\right)$$

91. The system of claim 90 wherein $E_{Coulomb}\left(mol.atom, msp^3\right)$ is one of is one of $E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$, $E_{Coulomb}\left(C_{ethane}, 2sp^3\right)$, $E_{Coulomb}\left(C_{acetylene}, 2sp^3\right)$, and $E_{Coulomb}\left(C_{alkane}, 2sp^3\right)$;

$E_{Coulomb}\left(atom, msp^3\right)$ is one of $E_{Coulomb}\left(C, 2sp^3\right)$ and $E_{Coulomb}\left(Cl, 3sp^3\right)$;

$E\left(mol.atom, msp^3\right)$ is one of $E\left(C_{ethylene}, 2sp^3\right)$, $E\left(C_{ethane}, 2sp^3\right)$, $E\left(C_{acetylene}, 2sp^3\right)$ $E\left(C_{alkane}, 2sp^3\right)$;

$E\left(atom, msp^3\right)$ is one of and $E\left(C, 2sp^3\right)$ and $E\left(Cl, 3sp^3\right)$;

$E_T\left(atom-atom, msp^3\right)$ is one of $E\left(C-C, 2sp^3\right)$, $E\left(C=C, 2sp^3\right)$, and. $E\left(C\equiv C, 2sp^3\right)$;

atom msp^3 is one of $C2sp^3$, $Cl3sp^3$

$E_T\left(atom-atom(s_1), msp^3\right)$ is $E_T\left(C-C, 2sp^3\right)$ and $E_T\left(atom-atom(s_2), msp^3\right)$ is $E_T\left(C=C, 2sp^3\right)$, and

r_{msp^3} is one of r_{C2sp^3}, $r_{ethane2sp^3}$, $r_{ethylene2sp^3}$, $r_{acetylene2sp^3}$, $r_{alkane2sp^3}$, and r_{Cl3sp^3},

92. The system of claim 91 wherein the energy of the MO is matched to that of the outermost atomic orbital or hybridized orbital of a bonding atom in the case where a minimum energy is achieved with a direct bond to the AO or HO.

93. The system of claim 92 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o \sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}};$$

The potential energy of the two nuclei is

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_o \sqrt{a^2-b^2}};$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The energy, V_m, of the magnetic force between the electrons is

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms plus $E(AO)$:

$$E_T = V_e + T + V_m + V_p$$

$$E_T = -\frac{n_1 e^2}{8\pi\varepsilon_o \sqrt{a^2-b^2}} \left[c_1 c_2 \left(2 - \frac{a_0}{a}\right) \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} - 1 \right] + E(AO)$$

$$= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'} \left[c_1 c_2 \left(2 - \frac{a_0}{a}\right) \ln \frac{a+c'}{a-c'} - 1 \right] + E(AO)$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and $E(AO)$ is the energy of the at least one atomic orbital to which the MO is energy matched.

94. The system of claim 93 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}, \text{ and}$$

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc} + E(AO).$$

95. The system of claim 94 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2 - \frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_1 c_2 e^2}{4\pi\varepsilon_o a^3}}{m_e}}{m_e c^2}}\right] - n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\} + E(AO)$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and $E(AO)$ is the energy of the at least one atomic orbital to which the MO is energy matched.

96. The system of claim 95 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{ \frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2 \left(2 - \frac{a_0}{a}\right) \ln\frac{a+c'}{a-c'} - 1 \right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_1 c_2 e^2}{4\pi\varepsilon_o b^3}\, m_e}}{m_e c^2}} \right] - n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right\} + E(AO)$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and $E(AO)$ is the energy of the at least one atomic orbital or hybridized atomic orbital or said orbital or hybridized orbital and the energy change with the formation of the bond by one or more of the orbital electrons to match the energies of the said orbital and the MO.

97. The system of claim 96 wherein $E(AO)$, the energy of the at least one atomic orbital or hybridized atomic orbital or said orbital or hybridized orbital and the energy change with the formation of the bond by one or more of the orbital electrons to match the energies of the said orbital and the MO, is at least one from the group of

$E(AO) = E(O2p\ shell) = -E(ionization;\ O) = -13.6181\ eV$;

$E(AO) = E(N2p\ shell) = -E(ionization;\ N) = -14.53414\ eV$;

$E(AO) = E(C, 2sp^3) = -14.63489\ eV$;

$E_T(AO) = E_{Coulomb}(Cl, 3sp^3) = -14.60295\ eV$;

$E_T(AO) = E(ionization;\ C) + E(ionization;\ C^+)$;

$E_T(AO) = E(C_{ethane}, 2sp^3) = -15.35946\ eV$;

$E_T(AO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3)$;

$E_T(AO) = E(C, 2sp^3) - 2E_T(C = C, 2sp^3) = -14.63489\ eV - (-2.26758\ eV)$;

$E_T(AO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002\ eV$;

$E_T(AO) = E(C, 2sp^3) - 2E_T(C \equiv C, 2sp^3) = -14.63489\ eV - (-3.13026\ eV)$;

$E_T(AO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3)$;

$E_T(AO) = E(C, 2sp^3) - E_T(C = C, 2sp^3) = -14.63489\ eV - (-1.13379\ eV)$, and $E_T(AO) = E(C_{alkane}, 2sp^3) = -15.56407\ eV$, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

98. The system of claim 97 wherein $c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2k' a}} = \sqrt{\frac{aa_0}{2k'}}$ is substituted into E_T to give

$$E_T = -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} - 1\right] + E(AO)$$

$$= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] + E(AO)$$

$$= -\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2k'}}}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2k'}}}{a-\sqrt{\frac{aa_0}{2k'}}} - 1\right] + E(AO)$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and $E(AO)$ is the energy of the at least one atomic orbital or hybridized atomic orbital to which the MO is energy matched.

99. The system of claim 98 wherein $E(basis\ energies)$ is given by the sum of a first integer q_1 times the total energy of H_2 and a second integer q_2 times the total energy of H, minus a third integer q_3 times the total energy of $E(AO)$ where the first integer can be 1,2,3..., and each of the second and third integers can be 0,1,2,3....

100. The system of claim 99 wherein E_T is set equal to $E(basis\ energies)$, and the semimajor axis a is solved.

101. The system of claim 100 wherein the semimajor axis a is solved from the equation of the form:

$$E_T = -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E(AO)$$

$$=-\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E(AO)$$

$$=-\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2k'}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2k'}}}{a-\sqrt{\frac{aa_0}{2k'}}}-1\right]+E(AO)=E(\textit{basis energies})$$

102. The system of claims 101 and 63 wherein the distance from the origin of the H_2-type-ellipsoidal-MO to each focus c', the internuclear distance $2c'$, and the length of the semiminor axis of the prolate spheroidal H_2-type MO $b=c$ are solved from the semimajor axis a.

103. The system of claims 102 where the number of equivalent bonds of the MO n_1 each comprising an H_2-type ellipsoidal MO is an integer greater than one.

104. The system of claims 103 where the fraction c_1 of a H_2-type ellipsoidal MO is 1. 0.75, 0.5, and 0.75/2.

105. The system of claims 104 where the factor c_2 of a H_2-type ellipsoidal MO is given by one of the list of 1 and the ratio of the ionization energy of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of H to meet the equipotential condition of the union of the H_2-type-ellipsoidal-MO and the AO of the atom, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

106. The system of claim 105 where the factor c_2 of a H_2-type ellipsoidal MO is 0.936127, the ratio of the ionization energy of N 14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.91771, the ratio of 14.82575 eV, $E_{Coulomb}\left(C,2sp^3\right)$ and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.93172, the ratio of 14.60295 eV, $E_{Coulomb}\left(Cl,3sp^3\right)$ given by Eq. (13.759), and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.87495, the ratio of 15.55033 eV, $E_{Coulomb}\left(C_{ethane},2sp^3\right)$ and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.85252, the ratio of 15.95955 eV, $E_{Coulomb}\left(C_{ethylene},2sp^3\right)$ and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.85252, the ratio of 15.95955 eV, $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ and 13.605804 eV, the Coulombic energy between the electron and proton of H, or

0.86359, the ratio of 15.55033 eV, $E_{Coulomb}\left(C_{alkane},2sp^3\right)$ and 13.605804 eV, the Coulombic energy between the electron and proton of H, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

107. The system of claim 106 where the fraction c_1 of a H_2-type ellipsoidal MO is such that the orbital energy E for each elliptical cross section of the prolate spheroidal MO is given by the sum of the kinetic T and potential V energies; $E=T+V$ is constant; the orbit is closed such that $T<|V|$; the time average of the kinetic energy, $<T>$, for elliptic motion in an inverse-squared field is $1/2$ that of the time average of the magnitude of the potential energy, $|<V>|$ ($<T>=1/2|<V>|$), and in the case that the energy of the MO is matched to at least one atomic orbital (AO), $E=T+V$, and for all points on the AO, $|E|=T=1/2|V|$.

108. The system of claim 107 where the energy of the MO is matched to at least one atomic orbital (AO) such that $E=T+V$, and for all points on the AO, $|E|=T=1/2|V|$.

109. A system of claim 108 of computing and rendering the nature of bound atomic and atomic ionic electrons from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration, comprising:

processing means for processing and solving the equations for charge, mass, and current density functions of electron(s) in a selected atom or ion, wherein the equations are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration; and

a display in communication with the processing means for displaying the current and charge density representation of the electron(s) of the selected atom or ion.

110. The system of claim 109 wherein the physical, Maxwellian solutions of the charge, mass, and current density functions of atoms and atomic ions comprises a solution of the classical wave equation $\left[\nabla^2 - \frac{1}{v^2}\frac{\delta^2}{\delta t^2}\right]\rho(r,\theta,\phi,t) = 0$ which is the equation of motion of the charge.

111. The system of claim 110, wherein the time, radial, and angular solutions of the wave equation are separable.

112. The system of claim 111, wherein the boundary constraint of the wave equation solution is nonradiation according to Maxwell's equations.

113. The system of claim 112, wherein a radial function that satisfies the boundary condition is a radial delta function

$$f(r) = \frac{1}{r^2}\delta(r - r_n).$$

114. The system of claim 113, wherein the boundary condition is met for a time harmonic function when the relationship between an allowed radius and the electron wavelength is given by

$$2\pi r_n = \lambda_n,$$

$$\omega = \frac{\hbar}{m_e r^2}, \text{ and}$$

$$v = \frac{\hbar}{m_e r}$$

where ω is the angular velocity of each point on the electron surface, v is the velocity of each point on the electron surface, and r is the radius of the electron.

115. The system of claim 114, wherein the spin function is given by the uniform function $Y_0^0(\phi,\theta)$ comprising angular momentum components of $\mathbf{L}_{xy}=\frac{\hbar}{4}$ and $\mathbf{L}_z=\frac{\hbar}{2}$.

116. The system of claim 115, wherein the atomic and atomic ionic charge and current density functions of bound electrons are described by a charge-density (mass-density) function which is the product of a radial delta function, two angular functions (spherical harmonic functions), and a time harmonic function:

$$\rho(r,\theta,\phi,t)=f(r)A(\theta,\phi,t)=\frac{1}{r^2}\delta(r-r_n)A(\theta,\phi,t); \qquad A(\theta,\phi,t)=Y(\theta,\phi)k(t)$$

wherein the spherical harmonic functions correspond to a traveling charge density wave confined to the spherical shell which gives rise to the phenomenon of orbital angular momentum.

117. The system of claim 116, wherein based on the radial solution, the angular charge and current-density functions of the electron, $A(\theta,\phi,t)$, must be a solution of the wave equation in two dimensions (plus time),

$$\left[\nabla^2-\frac{1}{v^2}\frac{\delta^2}{\delta t^2}\right]A(\theta,\phi,t)=0$$

where $\rho(r,\theta,\phi,t)=f(r)A(\theta,\phi,t)=\frac{1}{r^2}\delta(r-r_n)A(\theta,\phi,t)$ and $A(\theta,\phi,t)=Y(\theta,\phi)k(t)$

$$\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi}+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta}-\frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right]A(\theta,\phi,t)=0$$

where v is the linear velocity of the electron.

118. The system of claim 117, wherein the charge-density functions including the time-function factor are

$\ell=0$

$$\rho(r,\theta,\phi,t)=\frac{e}{8\pi r^2}[\delta(r-r_n)]\left[Y_0^0(\theta,\phi)+Y_\ell^m(\theta,\phi)\right]$$

$\ell \neq 0$

$$\rho(r,\theta,\phi,t)=\frac{e}{4\pi r^2}[\delta(r-r_n)]\left[Y_0^0(\theta,\phi)+\mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\}\right]$$

where $Y_\ell^m(\theta,\phi)$ are the spherical harmonic functions that spin about the z-axis with angular frequency ω_n with $Y_0^0(\theta,\phi)$ the constant function

$\mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\}=P_\ell^m(\cos\theta)\cos\left(m\phi+\omega_n' t\right)$ where to keep the form of the spherical harmonic as a traveling wave about the z-axis, $\omega_n'=m\omega_n$.

119. The system of claim 118, wherein the spin and angular moment of inertia, I, angular momentum, L, and energy, E, for quantum number ℓ are given by

$\ell = 0$

$$I_z = I_{spin} = \frac{m_e r_n^2}{2}$$

$$L_z = I\omega \mathbf{i}_z = \pm\frac{\hbar}{2}$$

$$E_{rotational} = E_{rotational,\,spin} = \frac{1}{2}\left[I_{spin}\left(\frac{\hbar}{m_e r_n^2}\right)^2\right] = \frac{1}{2}\left[\frac{m_e r_n^2}{2}\left(\frac{\hbar}{m_e r_n^2}\right)^2\right] = \frac{1}{4}\left[\frac{\hbar^2}{2I_{spin}}\right]$$

$\ell \neq 0$

$$I_{orbital} = m_e r_n^2\left[\frac{\ell(\ell+1)}{\ell^2+\ell+1}\right]^{\frac{1}{2}}$$

$$L_z = m\hbar$$

$$L_{z\ total} = L_{z\ spin} + L_{z\ orbital}$$

$$E_{rotational,\,orbital} = \frac{\hbar^2}{2I}\left[\frac{\ell(\ell+1)}{\ell^2+2\ell+1}\right]$$

$$T = \frac{\hbar^2}{2m_e r_n^2}$$

$$\left\langle E_{rotational,\,orbital}\right\rangle = 0\,.$$

120. The system of claim 119, wherein the force balance equation for one-electron atoms and ions is

$$\frac{m_e}{4\pi r_1^2}\frac{v_1^2}{r_1} = \frac{e}{4\pi r_1^2}\frac{Ze}{4\pi\varepsilon_o r_1^2} - \frac{1}{4\pi r_1^2}\frac{\hbar^2}{m_p r_n^3}$$

$$r_1 = \frac{a_H}{Z}$$

where a_H is the radius of the hydrogen atom.

121. The system of claim 120, wherein from Maxwell's equations, the potential energy V, kinetic energy T, electric energy or binding energy E_{ele} are

$$V = \frac{-Ze^2}{4\pi\varepsilon_o r_1} = \frac{-Z^2e^2}{4\pi\varepsilon_o a_H} = -Z^2\ X\ 4.3675\ X\ 10^{-18}\ J = -Z^2\ X\ 27.2\ eV$$

$$T = \frac{Z^2e^2}{8\pi\varepsilon_o a_H} = Z^2\ X\ 13.59\ eV$$

$$T = E_{ele} = -\frac{1}{2}\varepsilon_o\int_{\infty}^{r_1}\mathbf{E}^2 dv \quad \text{where } \mathbf{E} = -\frac{Ze}{4\pi\varepsilon_o r^2}$$

$$E_{ele} = -\frac{Z^2e^2}{8\pi\varepsilon_o a_H} = -Z^2\ X\ 2.1786\ X\ 10^{-18}\ J = -Z^2\ X\ 13.598\ eV\,,$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

122. The system of claim 121, wherein the force balance equation solution of two electron atoms is a central force balance equation with the nonradiation condition is given by

$$\frac{m_e}{4\pi r_2^2}\frac{v_2^2}{r_2} = \frac{e}{4\pi r_2^2}\frac{(Z-1)e}{4\pi\varepsilon_o r_2^2} + \frac{1}{4\pi r_2^2}\frac{\hbar^2}{Zm_e r_2^3}\sqrt{s(s+1)}$$

which gives the radius of both electrons as

$$r_2 = r_1 = a_0\left(\frac{1}{Z-1} - \frac{\sqrt{s(s+1)}}{Z(Z-1)}\right);\ s = \frac{1}{2}.$$

123. The system of claim 122, wherein the ionization energy for helium, which has no electric field beyond r_1 is given by

$$Ionization\ Energy(He) = -E(electric) + E(magnetic)$$

where,

$$E(electric) = -\frac{(Z-1)e^2}{8\pi\varepsilon_o r_1}$$

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_1^3}$$

For $3 \le Z$

$$Ionization\ Energy = -Electric\ Energy - \frac{1}{Z}Magnetic\ Energy.$$

124. The system of claim 123, wherein the electrons of multielectron atoms all exist as orbitspheres of discrete radii which are given by r_n of the radial Dirac delta function, $\delta(r-r_n)$.

125. The system of claim 124, wherein electron orbitspheres may be spin paired or unpaired depending on the force balance which applies to each electron wherein the electron configuration is a minimum of energy.

126. The system of claim 125, wherein the minimum energy configurations are given by solutions to Laplace's equation.

127. The system of claim 126, wherein the electrons of an atom with the same principal and ℓ quantum numbers align parallel until each of the m_ℓ levels are occupied, and then pairing occurs until each of the m_ℓ levels contain paired electrons.

128. The system of claim 127, wherein the electron configuration for one through twenty-electron atoms that achieves an energy minimum is: $1s < 2s < 2p < 3s < 3p < 4s$.

129. The system of claim 128, wherein the corresponding force balance of the central Coulombic, paramagnetic, and diamagnetic forces was derived for each n-electron atom that was solved for the radius of each electron.

130. The system of claim 129, wherein the central Coulombic force is that of a point charge at the origin since the electron charge-density functions are spherically symmetrical with a time dependence that is nonradiative.

131. The system of claim 130, wherein the ionization energies are obtained using the calculated radii in the determination of the Coulombic and any magnetic energies.

132. The system of claim 131, wherein the general equation for the radii of s electrons is given by

$$r_n = \frac{\dfrac{a_0\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)} \pm a_0\sqrt{\left(\dfrac{\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]Er_m\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)}}}{2}$$

r_m *in units of* a_0

where positive root must be taken in order that $r_n > 0$;

Z is the nuclear charge, n is the number of electrons,

r_m is the radius of the proceeding filled shell(s) given by

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$$r_n = \frac{\frac{a_0\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)} \pm a_0 \sqrt{\left(\frac{\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]Er_m\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)}}}{2}$$

r_m *in units of* a_0

for the preceding s shell(s);

$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}}}{2}$$

r_3 *in units of* a_0

for the 2p shell, and

$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)r_{12}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

r_{12} *in units of* a_0

for the 3p shell;

the parameter A corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic}$:

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_e r_3^2 r_1}\sqrt{s(s+1)}\mathbf{i}_r;$$

the parameter B corresponds to the paramagnetic force, $\mathbf{F}_{mag\ 2}$:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_1 r_4^2}\sqrt{s(s+1)}\mathbf{i}_r;$$

the parameter C corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic\ 3}$:

$$\mathbf{F}_{diamagnetic\ 3} = -\frac{1}{Z}\frac{8\hbar^2}{m_e r_{11}^3}\sqrt{s(s+1)}\mathbf{i}_r;$$

the parameter D corresponds to the paramagnetic force, $\mathbf{F}_{mag}$:

$$\mathbf{F}_{mag} = \frac{1}{4\pi r_2^2}\frac{1}{Z}\frac{\hbar^2}{m_e r^3}\sqrt{s(s+1)}, \text{ and}$$

the parameter E corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, due to a relativistic effect with an electric field for $r > r_n$:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{m_e r_3^4}10\sqrt{3/4}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-11}{Z-10}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{11}^4}10\sqrt{s(s+1)}\mathbf{i}_r, \text{ and}$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r.$$

wherein the parameters of atoms filling the 1s, 2s, 3s, and 4s orbitals are

Atom Type	Electron Configuration	Ground State Term	Orbital Arrangement of s Electrons (s state)	Diamag. Force Factor *A*	Paramag. Force Factor *B*	Diamag. Force Factor *C*	Paramag. Force Factor *D*	Diamag. Force Factor *E*
Neutral 1 e Atom *H*	$1s^1$	$^2S_{1/2}$	↑ 1s	0	0	0	0	0
Neutral 2 e Atom *He*	$1s^2$	$^1S_0$	↑ ↓ 1s	0	0	0	1	0
Neutral 3 e Atom *Li*	$2s^1$	$^2S_{1/2}$	↑ 2s	1	0	0	0	0
Neutral 4 e Atom *Be*	$2s^2$	$^1S_0$	↑ ↓ 2s	1	0	0	1	0
Neutral 11 e Atom *Na*	$1s^2 2s^2 2p^6 3s^1$	$^2S_{1/2}$	↑ 3s	1	0	8	0	0
Neutral 12 e Atom *Mg*	$1s^2 2s^2 2p^6 3s^2$	$^1S_0$	↑ ↓ 3s	1	3	12	1	0
Neutral 19 e Atom	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$^2S_{1/2}$	↑ 4s	2	0	12	0	0

K								
Neutral	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$^1S_0$	$\underline{\uparrow\downarrow}$ 4s	1	3	24	1	0
20 e Atom								
Ca								
1 e Ion	$1s^1$	$^2S_{1/2}$	$\underline{\uparrow}$ 1s	0	0	0	0	0
2 e Ion	$1s^2$	$^1S_0$	$\underline{\uparrow\downarrow}$ 1s	0	0	0	1	0
3 e Ion	$2s^1$	$^2S_{1/2}$	$\underline{\uparrow}$ 2s	1	0	0	0	1
4 e Ion	$2s^2$	$^1S_0$	$\underline{\uparrow\downarrow}$ 2s	1	0	0	1	1
11 e Ion	$1s^2 2s^2 2p^6 3s^1$	$^2S_{1/2}$	$\underline{\uparrow}$ 3s	1	4	8	0	$1+\frac{\sqrt{2}}{2}$
12 e Ion	$1s^2 2s^2 2p^6 3s^2$	$^1S_0$	$\underline{\uparrow\downarrow}$ 3s	1	6	0	0	$1+\frac{\sqrt{2}}{2}$
19 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$^2S_{1/2}$	$\underline{\uparrow}$ 4s	3	0	24	0	$2-\sqrt{2}$
20 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$^1S_0$	$\underline{\uparrow\downarrow}$ 4s	2	0	24	0	$2-\sqrt{2}$

133. The system of claim 132, with the radii, r_n, wherein the ionization energy for atoms having an outer s-shell are given by the negative of the electric energy, $E(electric)$, given by:

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}$$

except that minor corrections due to the magnetic energy must be included in cases wherein the s electron does not couple to p electrons as given by

$$Ionization\ Energy(He) = -E(electric) + E(magnetic)\left(1-\frac{1}{2}\left(\left(\frac{2}{3}\cos\frac{\pi}{3}\right)^2+\alpha\right)\right)$$

$$Ionization\ Energy = -Electric\ Energy - \frac{1}{Z}Magnetic\ Energy$$

$$E(ionization;\ Li) = \frac{(Z-2)e^2}{8\pi\varepsilon_o r_3} + \Delta E_{mag}$$
$$= 5.3178\ eV + 0.0860\ eV = 5.4038\ eV$$

$$E(Ionization) = E(Electric) + E_T$$

$$E(ionization;\ Be) = \frac{(Z-3)e^2}{8\pi\varepsilon_o r_4} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_4^3} + \Delta E_{mag}$$, and
$$= 8.9216\ eV + 0.03226\ eV + 0.33040\ eV = 9.28430\ eV$$

$E(Ionization) = -Electric\ Energy - \frac{1}{Z}Magnetic\ Energy - E_T$, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

134. The system of claim 133, wherein the radii and energies of the 2p electrons are solved using the forces given by

$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}\frac{\hbar^2}{4m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r,$$

and the radii r_3 are given by

$$r_4 = r_3 = \frac{\left(\frac{a_0\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)} \pm a_o\sqrt{\frac{\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2}+4\frac{\left[\frac{Z-3}{Z-2}\right]r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}}\right)}{2}$$

r_1 in units of a_o

135. The system of claim 134, wherein the electric energy given by

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}$$

gives the corresponding ionization energies.

136. The system of claim 135, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration $1s^2 2s^2 2p^{n-4}$, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by:

$$r_1 = r_2 = a_o\left[\frac{1}{Z-1}-\frac{\sqrt{\frac{3}{4}}}{Z(Z-1)}\right];$$

two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by:

$$r_4 = r_3 = \frac{\left(\frac{a_0\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)} \pm a_o \sqrt{\frac{\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2} + 4\frac{\left[\frac{Z-3}{Z-2}\right] r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}} \right)}{2}$$

r_1 *in units of* a_o

and $n-4$ electrons in an orbitsphere with radius r_n given by

$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)^2} + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}}}{2}$$

r_3 *in units of* a_0

the positive root must be taken in order that $r_n > 0$;

the parameter A corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic}$:

$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!} \frac{\hbar^2}{4m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r ;$$

and the parameter B corresponds to the paramagnetic force, $\mathbf{F}_{mag\ 2}$:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r ,$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r , \text{ and}$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r$$

wherein the parameters of five through ten-electron atoms are

Atom Type	Electron Configuration	Ground State Term	Orbital Arrangement of 2p Electrons (2p state)	Diamagnetic Force Factor A	Paramagnetic Force Factor B
Neutral 5 e Atom B	$1s^2 2s^2 2p^1$	$^2P^0_{1/2}$	$\underline{\uparrow}\ \underline{\ \ }\ \underline{\ \ }$ 1 0 -1	2	0
Neutral 6 e Atom C	$1s^2 2s^2 2p^2$	$^3P_0$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\ \ }$ 1 0 -1	$\frac{2}{3}$	0
Neutral 7 e Atom N	$1s^2 2s^2 2p^3$	$^4S^0_{3/2}$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{1}{3}$	1
Neutral 8 e Atom O	$1s^2 2s^2 2p^4$	$^3P_2$	$\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$ 1 0 -1	1	2
Neutral 9 e Atom F	$1s^2 2s^2 2p^5$	$^2P^0_{3/2}$	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{2}{3}$	3
Neutral 10 e Atom Ne	$1s^2 2s^2 2p^6$	$^1S_0$	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$ 1 0 -1	0	3
5 e Ion	$1s^2 2s^2 2p^1$	$^2P^0_{1/2}$	$\underline{\uparrow}\ \underline{\ \ }\ \underline{\ \ }$ 1 0 -1	$\frac{5}{3}$	1
6 e Ion	$1s^2 2s^2 2p^2$	$^3P_0$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\ \ }$ 1 0 -1	$\frac{5}{3}$	4
7 e Ion	$1s^2 2s^2 2p^3$	$^4S^0_{3/2}$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{5}{3}$	6

8 e Ion	$1s^2 2s^2 2p^4$	$^3P_2$	$\underline{\uparrow\downarrow}_{1}\ \underline{\uparrow}_{0}\ \underline{\uparrow}_{-1}$	$\frac{5}{3}$	6
9 e Ion	$1s^2 2s^2 2p^5$	$^2P^0_{3/2}$	$\underline{\uparrow\downarrow}_{1}\ \underline{\uparrow\downarrow}_{0}\ \underline{\uparrow}_{-1}$	$\frac{5}{3}$	9
10 e Ion	$1s^2 2s^2 2p^6$	$^1S_0$	$\underline{\uparrow\downarrow}_{1}\ \underline{\uparrow\downarrow}_{0}\ \underline{\uparrow\downarrow}_{-1}$	$\frac{5}{3}$	12

137. The system of claim 136, wherein the ionization energy for the boron atom is given by

$$E(ionization;\ B) = \frac{(Z-4)e^2}{8\pi\varepsilon_o r_5} + \Delta E_{mag}$$
$$= 8.147170901\ eV + 0.15548501\ eV = 8.30265592\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

138. The system of claim 137, wherein the ionization energies for the n-electron atoms having the radii, r_n ,are given by the negative of the electric energy, $E(electric)$, given by

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}.$$

139. The system of claim 138, wherein the radii of the 3p electrons are given using the forces given by

$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}+\frac{2}{3}+\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2}=\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2}=(4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r=\frac{1}{Z}\frac{12\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2}=\frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2}=\frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2}=\frac{1}{Z}\frac{8\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

and the radii r_{12} are given by

$$r_{12}=\frac{\dfrac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}\pm a_0\sqrt{\left(\dfrac{1}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}\right)^2+\dfrac{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}}}{2}$$

r_{10} *in units of* a_0

140. The system of claim 139, wherein the ionization energies are given by electric energy given by:

$$E(Ionization)=-Electric\ Energy=\frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}.$$

141. The system of claim 140, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration $1s^2 2s^2 2p^6 3s^2 3p^{n-12}$, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by:

$$r_1 = r_2 = a_o \left[\frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right]$$

two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by:

$$r_4 = r_3 = \frac{\left(\frac{a_0 \left(1 - \frac{\sqrt{\frac{3}{4}}}{Z} \right)}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)} \pm a_o \sqrt{\frac{\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z} \right)^2}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)^2} + 4 \frac{\left[\frac{Z-3}{Z-2} \right] r_1 10 \sqrt{\frac{3}{4}}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)}} \right)}{2}$$

r_1 *in units of* a_o

three sets of paired indistinguishable electrons in an orbitsphere with radius r_{10} given by:

$$r_{10} = \frac{\frac{a_0}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \pm a_0 \sqrt{\frac{1}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)^2} + \frac{20\sqrt{3} \left(\left[\frac{Z-10}{Z-9} \right] \left(1 - \frac{\sqrt{2}}{2} \right) r_3 \right)}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)}}}{2}$$

r_3 *in units of* a_0

two indistinguishable spin-paired electrons in an orbitsphere with radius r_{12} given by:

$$r_{12} = \frac{\frac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}}}{2}$$

r_{10} *in units of* a_0

and $n-12$ electrons in a 3p orbitsphere with radius r_n given by

$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)r_{12}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

r_{12} *in units of* a_0

where the positive root must be taken in order that $r_n > 0$;

the parameter A corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic}$:

$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$, and the parameter B corresponds to the paramagnetic force, $\mathbf{F}_{mag\ 2}$:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r, \text{ and}$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{8\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

wherein the parameters of thirteen through eighteen-electron atoms are

Atom Type	Electron Configuration	Ground State Term	Orbital Arrangement of 3p Electrons (3p state)	Diamagnetic Force Factor *A*	Paramagnetic Force Factor *B*
Neutral 13 e Atom *Al*	$1s^2 2s^2 2p^6 3s^2 3p^1$	$^2P^0_{1/2}$	$\underline{\uparrow}_1 \quad \underline{\quad}_0 \quad \underline{\quad}_{-1}$	$\frac{11}{3}$	0
Neutral 14 e Atom *Si*	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_0$	$\underline{\uparrow}_1 \quad \underline{\uparrow}_0 \quad \underline{\quad}_{-1}$	$\frac{7}{3}$	0
Neutral 15 e Atom *P*	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^4S^0_{3/2}$	$\underline{\uparrow}_1 \quad \underline{\uparrow}_0 \quad \underline{\uparrow}_{-1}$	$\frac{5}{3}$	2
Neutral 16 e Atom *S*	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_2$	$\underline{\uparrow\downarrow}_1 \quad \underline{\uparrow}_0 \quad \underline{\uparrow}_{-1}$	$\frac{4}{3}$	1
Neutral 17 e Atom *Cl*	$1s^2 2s^2 2p^6 3s^2 3p^5$	$^2P^0_{3/2}$	$\underline{\uparrow\downarrow}_1 \quad \underline{\uparrow\downarrow}_0 \quad \underline{\uparrow}_{-1}$	$\frac{2}{3}$	2
Neutral 18 e Atom *Ar*	$1s^2 2s^2 2p^6 3s^2 3p^6$	$^1S_0$	$\underline{\uparrow\downarrow}_1 \quad \underline{\uparrow\downarrow}_0 \quad \underline{\uparrow\downarrow}_{-1}$	$\frac{1}{3}$	4
13 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^1$	$^2P^0_{1/2}$	$\underline{\uparrow}_1 \quad \underline{\quad}_0 \quad \underline{\quad}_{-1}$	$\frac{5}{3}$	12

14 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_0$	$\underline{\uparrow}$ 1	$\underline{\uparrow}$ 0	$\underline{\quad}$ -1	$\frac{1}{3}$	16
15 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^4S^0_{3/2}$	$\underline{\uparrow}$ 1	$\underline{\uparrow}$ 0	$\underline{\uparrow}$ -1	0	24
16 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_2$	$\underline{\uparrow\downarrow}$ 1	$\underline{\uparrow}$ 0	$\underline{\uparrow}$ -1	$\frac{1}{3}$	24
17 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^5$	$^2P^0_{3/2}$	$\underline{\uparrow\downarrow}$ 1	$\underline{\uparrow\downarrow}$ 0	$\underline{\uparrow}$ -1	$\frac{2}{3}$	32
18 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^6$	$^1S_0$	$\underline{\uparrow\downarrow}$ 1	$\underline{\uparrow\downarrow}$ 0	$\underline{\uparrow\downarrow}$ -1	0	40

142. The system of claim 141, wherein the ionization energies for the n-electron 3p atoms are given by electric energy given by:

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}.$$

143. The system of claim 142, wherein the ionization energy for the aluminum atom is given by

$$E(ionization;\ Al) = \frac{(Z-12)e^2}{8\pi\varepsilon_o r_{13}} + \Delta E_{mag}$$
$$= 5.95270\ eV + 0.031315\ eV = 5.98402\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

144. A system of claim 1 of computing the nature of bound atomic and atomic ionic electrons from physical solutions of the charge, mass, and current density functions of atoms

and atomic ions, which solutions are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration, comprising:

processing means for processing and solving the equations for charge, mass, and current density functions of electron(s) in selected atoms or ions, wherein the equations are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration; and

output means for outputting the solutions of the charge, mass, and current density functions of the atoms and atomic ions.

145. A system of claim 1 comprising the steps of;

a.) inputting electron functions that are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration;

b.) inputting a trial electron configuration;

c.) inputting the corresponding centrifugal, Coulombic, diamagnetic and paramagnetic forces,

d.) forming the force balance equation comprising the centrifugal force equal to the sum of the Coulombic, diamagnetic and paramagnetic forces;

e.) solving the force balance equation for the electron radii;

f.) calculating the energy of the electrons using the radii and the corresponding electric and magnetic energies;

g.) repeating Steps a-f for all possible electron configurations, and

h.) outputting the lowest energy configuration and the corresponding electron radii for that configuration.

146. The system of claim 145, wherein the output is rendered using the electron functions.

147. The system of claim 146, wherein the electron functions are given by at least one of the group comprising:

$\ell = 0$

$$\rho(r,\theta,\phi,t) = \frac{e}{8\pi r^2}[\delta(r-r_n)]\left[Y_0^0(\theta,\phi) + Y_\ell^m(\theta,\phi)\right]$$

$\ell \neq 0$

$$\rho(r,\theta,\phi,t) = \frac{e}{4\pi r^2}[\delta(r-r_n)]\left[Y_0^0(\theta,\phi) + \mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\}\right]$$

where $Y_\ell^m(\theta,\phi)$ are the spherical harmonic functions that spin about the z-axis with angular frequency ω_n with $Y_0^0(\theta,\phi)$ the constant function. $\mathrm{Re}\left\{Y_\ell^m(\theta,\phi)e^{i\omega_n t}\right\} = P_\ell^m(\cos\theta)\cos\left(m\phi + \omega_n' t\right)$ where to keep the form of the spherical harmonic as a traveling wave about the z-axis, $\omega_n' = m\omega_n$.

148. The system of claim 147, wherein the forces are given by at least one of the group comprising:

$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2}\mathbf{i}_r$$

$$\mathbf{F}_{ele} = \frac{(Z-(n-1))e^2}{4\pi\varepsilon_o r_n^2}\mathbf{i}_r$$

$$\mathbf{F}_{mag} = \frac{1}{4\pi r_2^{\,2}}\frac{1}{Z}\frac{\hbar^2}{m_e r^3}\sqrt{s(s+1)}$$

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_e r_3^2 r_1}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}\frac{\hbar^2}{4m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}+\frac{2}{3}+\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{m_e r_3^4}10\sqrt{3/4}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-11}{Z-10}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{11}^4}10\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 3} = -\frac{1}{Z}\frac{8\hbar^2}{m_e r_{11}^{\ 3}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_1 r_4^2}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r, \text{ and}$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{8\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

149. The system of claim 148, wherein the radii are given by at least one of the group comprising:

$$r_1 = r_2 = a_o\left[\frac{1}{Z-1}-\frac{\sqrt{\frac{3}{4}}}{Z(Z-1)}\right]$$

$$r_4 = r_3 = \frac{\dfrac{a_0\left(1-\dfrac{\sqrt{\frac{3}{4}}}{Z}\right)}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)} \pm a_o \sqrt{\dfrac{\left(1-\dfrac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2} + 4\dfrac{\left[\frac{Z-3}{Z-2}\right] r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}}}{2}$$

r_1 in units of a_o

$$r_n = \frac{\dfrac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\left(\dfrac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}}}{2}$$

r_3 in units of a_0

$$r_{10} = \frac{\dfrac{a_0}{\left((Z-9)-\left(\frac{5}{24}-\frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\left(\dfrac{1}{\left((Z-9)-\left(\frac{5}{24}-\frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\frac{Z-10}{Z-9}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-9)-\left(\frac{5}{24}-\frac{6}{Z}\right)\frac{\sqrt{3}}{r_3}\right)}}}{2}$$

r_3 in units of a_0

$$r_{11} = \frac{a_0\left(1+\frac{8}{Z}\sqrt{\frac{3}{4}}\right)}{(Z-10)-\frac{\sqrt{\frac{3}{4}}}{4r_{10}}}, \; r_{10} \text{ in units of } a_0$$

$$r_{12} = \frac{\frac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}}}{2}$$

r_{10} *in units of* a_0

$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)r_{12}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

r_{12} *in units of* a_0

$$r_n = \frac{\frac{a_0\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)} \pm a_0 \sqrt{\left(\frac{\left(1+(C-D)\frac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]Er_m\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_m}\right)}}}{2}$$

r_m *in units of* a_0

150. The system of claim 149, wherein the electric energy of each electron of radius r_n is given by at least one of the group comprising:

$$E(electric) = -\frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}$$

$$Ionization\ Energy(He) = -E(electric) + E(magnetic)\left(1-\frac{1}{2}\left(\left(\frac{2}{3}\cos\frac{\pi}{3}\right)^2+\alpha\right)\right)$$

$$Ionization\ Energy = -Electric\ Energy - \frac{1}{Z}Magnetic\ Energy$$

$$E(Ionization) = -Electric\ Energy - \frac{1}{Z}Magnetic\ Energy - E_T$$

$$E(ionization;\ Li) = \frac{(Z-2)e^2}{8\pi\varepsilon_o r_3} + \Delta E_{mag}$$
$$= 5.3178\ eV + 0.0860\ eV = 5.4038\ eV$$

$$E(ionization;\ B) = \frac{(Z-4)e^2}{8\pi\varepsilon_o r_5} + \Delta E_{mag}$$
$$= 8.147170901\ eV + 0.15548501\ eV = 8.30265592\ eV$$

$$E(ionization;\ Be) = \frac{(Z-3)e^2}{8\pi\varepsilon_o r_4} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_4^3} + \Delta E_{mag}$$
$$= 8.9216\ eV + 0.03226\ eV + 0.33040\ eV = 9.28430\ eV$$

$$E(ionization;\ Na) = -Electric\ Energy = \frac{(Z-10)e^2}{8\pi\varepsilon_o r_{11}} = 5.12592\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

151. The system of claim 150, wherein the radii of s electrons are given by

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$$r_n = \frac{\dfrac{a_0\left(1+(C-D)\dfrac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)} \pm a_0 \sqrt{\left(\dfrac{\left(1+(C-D)\dfrac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-n}{Z-(n-1)}\right]Er_m\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)}}}{2}$$

r_m *in units of* a_0

where positive root must be taken in order that $r_n > 0$;

Z is the nuclear charge, n is the number of electrons,

r_m is the radius of the proceeding filled shell(s) given by

$$r_n = \frac{\dfrac{a_0\left(1+(C-D)\dfrac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)} \pm a_0 \sqrt{\left(\dfrac{\left(1+(C-D)\dfrac{\sqrt{3}}{2Z}\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\dfrac{Z-n}{Z-(n-1)}\right]Er_m\right)}{\left((Z-(n-1))-\left(\dfrac{A}{8}-\dfrac{B}{2Z}\right)\dfrac{\sqrt{3}}{r_m}\right)}}}{2}$$

r_m *in units of* a_0

for the preceding s shell(s);

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$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}}}{2}$$

r_3 *in units of* a_0

for the 2p shell, and

$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)r_{12}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

r_{12} *in units of* a_0

for the 3p shell;

the parameter A corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic}$:

$$\mathbf{F}_{diamagnetic} = -\frac{\hbar^2}{4m_e r_3^2 r_1}\sqrt{s(s+1)}\mathbf{i}_r;$$

the parameter B corresponds to the paramagnetic force, $\mathbf{F}_{mag\ 2}$:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_1 r_4^2}\sqrt{s(s+1)}\mathbf{i}_r;$$

the parameter C corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic\ 3}$:

$$\mathbf{F}_{diamagnetic\ 3} = -\frac{1}{Z}\frac{8\hbar^2}{m_e r_{11}^3}\sqrt{s(s+1)}\mathbf{i}_r;$$

the parameter D corresponds to the paramagnetic force, $\mathbf{F}_{mag}$:

$$\mathbf{F}_{mag} = \frac{1}{4\pi r_2^2}\frac{1}{Z}\frac{\hbar^2}{m_e r^3}\sqrt{s(s+1)}\,, \text{ and}$$

the parameter E corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic\ 2}$, due to a relativistic effect with an electric field for $r > r_n$:

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-3}{Z-2}\right]\frac{r_1\hbar^2}{m_e r_3^4}10\sqrt{3/4}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-11}{Z-10}\right]\left(1+\frac{\sqrt{2}}{2}\right)\frac{r_{10}\hbar^2}{m_e r_{11}^4}10\sqrt{s(s+1)}\mathbf{i}_r\,, \text{ and}$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)\frac{r_{18}\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r\,.$$

wherein the parameters of atoms filling the 1s, 2s, 3s, and 4s orbitals are

Atom Type	Electron Configuration	Ground State Term	Orbital Arrangement of s Electrons (s state)	Dia mag. Force Factor *A*	Para mag. Force Factor *B*	Dia mag. Force Factor *C*	Para mag. Force Factor *D*	Diamag. Force Factor *E*
Neutral 1 e Atom *H*	$1s^1$	$^2S_{1/2}$	↑ 1s	0	0	0	0	0
Neutral 2 e Atom *He*	$1s^2$	$^1S_0$	↑ ↓ 1s	0	0	0	1	0
Neutral 3 e Atom *Li*	$2s^1$	$^2S_{1/2}$	↑ 2s	1	0	0	0	0
Neutral 4 e Atom *Be*	$2s^2$	$^1S_0$	↑ ↓ 2s	1	0	0	1	0
Neutral 11 e Atom *Na*	$1s^2 2s^2 2p^6 3s^1$	$^2S_{1/2}$	↑ 3s	1	0	8	0	0
Neutral 12 e Atom *Mg*	$1s^2 2s^2 2p^6 3s^2$	$^1S_0$	↑ ↓ 3s	1	3	12	1	0

Neutral 19 e Atom *K*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$^2S_{1/2}$	↑ 4s	2	0	12	0	0
Neutral 20 e Atom *Ca*	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$^1S_0$	↑ ↓ 4s	1	3	24	1	0
1 e Ion	$1s^1$	$^2S_{1/2}$	↑ 1s	0	0	0	0	0
2 e Ion	$1s^2$	$^1S_0$	↑ ↓ 1s	0	0	0	1	0
3 e Ion	$2s^1$	$^2S_{1/2}$	↑ 2s	1	0	0	0	1
4 e Ion	$2s^2$	$^1S_0$	↑ ↓ 2s	1	0	0	1	1
11 e Ion	$1s^2 2s^2 2p^6 3s^1$	$^2S_{1/2}$	↑ 3s	1	4	8	0	$1+\frac{\sqrt{2}}{2}$
12 e Ion	$1s^2 2s^2 2p^6 3s^2$	$^1S_0$	↑ ↓ 3s	1	6	0	0	$1+\frac{\sqrt{2}}{2}$
19 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$^2S_{1/2}$	↑ 4s	3	0	24	0	$2-\sqrt{2}$
20 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$^1S_0$	↑ ↓ 4s	2	0	24	0	$2-\sqrt{2}$

152. The system of claim 151, with the radii, r_n, wherein the ionization energy for atoms having an outer s-shell are given by the negative of the electric energy, $E(electric)$, given by:

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}$$

except that minor corrections due to the magnetic energy must be included in cases wherein the s electron does not couple to p electrons as given by

$$Ionization\ Energy(He) = -E(electric) + E(magnetic)\left(1-\frac{1}{2}\left(\left(\frac{2}{3}\cos\frac{\pi}{3}\right)^2+\alpha\right)\right)$$

$$Ionization\ Energy = -Electric\ Energy - \frac{1}{Z}Magnetic\ Energy$$

$$E(ionization;\ Li) = \frac{(Z-2)e^2}{8\pi\varepsilon_o r_3} + \Delta E_{mag}$$
$$= 5.3178\ eV + 0.0860\ eV = 5.4038\ eV$$

$$E(Ionization) = E(Electric) + E_T$$

$$E(ionization;\ Be) = \frac{(Z-3)e^2}{8\pi\varepsilon_o r_4} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_4^3} + \Delta E_{mag}$$
$$= 8.9216\ eV + 0.03226\ eV + 0.33040\ eV = 9.28430\ eV$$

, and

$$E(Ionization) = -Electric\ Energy - \frac{1}{Z}Magnetic\ Energy - E_T$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

153. The system of claim 152, wherein the radii and energies of the 2p electrons are solved using the forces given by

$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}\frac{\hbar^2}{4m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r,$$

and the radii r_3 are given by

$$r_4 = r_3 = \frac{\left(\frac{a_0\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)} \pm a_o\sqrt{\frac{\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2}+4\frac{\left[\frac{Z-3}{Z-2}\right]r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}}\right)}{2}$$

r_1 *in units of* a_o

154. The system of claim 153, wherein the electric energy given by

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}$$

gives the corresponding ionization energies.

155. The system of claim 154, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration $1s^2 2s^2 2p^{n-4}$, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by:

$$r_1 = r_2 = a_o\left[\frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)}\right];$$

two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by:

$$r_4 = r_3 = \frac{\left(\frac{a_0\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)} \pm a_o\sqrt{\frac{\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2} + 4\frac{\left[\frac{Z-3}{Z-2}\right]r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}}\right)}{2}$$

r_1 *in units of* a_o

and $n-4$ electrons in an orbitsphere with radius r_n given by

$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)} \pm a_0\sqrt{\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_3}\right)}}}{2};$$

r_3 *in units of* a_0

the positive root must be taken in order that $r_n > 0$;

the parameter A corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic}$:

$$\mathbf{F}_{diamagnetic} = -\sum_{m} \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!} \frac{\hbar^2}{4m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r;$$

and the parameter B corresponds to the paramagnetic force, $\mathbf{F}_{mag\ 2}$:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r,$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{4\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r, \text{ and}$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z} \frac{\hbar^2}{m_e r_n^2 r_3} \sqrt{s(s+1)}\mathbf{i}_r.$$

wherein the parameters of five through ten-electron atoms are

Atom Type	Electron Configuration	Ground State Term	Orbital Arrangement of 2p Electrons (2p state)	Diamagnetic Force Factor A	Paramagnetic Force Factor B
Neutral 5 e Atom B	$1s^2 2s^2 2p^1$	$^2P^0_{1/2}$	$\underline{\uparrow}\ \underline{\ \ }\ \underline{\ \ }$ 1 0 -1	2	0
Neutral 6 e Atom C	$1s^2 2s^2 2p^2$	$^3P_0$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\ \ }$ 1 0 -1	$\frac{2}{3}$	0
Neutral 7 e Atom N	$1s^2 2s^2 2p^3$	$^4S^0_{3/2}$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{1}{3}$	1
Neutral 8 e Atom O	$1s^2 2s^2 2p^4$	$^3P_2$	$\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$ 1 0 -1	1	2
Neutral 9 e Atom F	$1s^2 2s^2 2p^5$	$^2P^0_{3/2}$	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{2}{3}$	3
Neutral 10 e Atom Ne	$1s^2 2s^2 2p^6$	$^1S_0$	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$ 1 0 -1	0	3
5 e Ion	$1s^2 2s^2 2p^1$	$^2P^0_{1/2}$	$\underline{\uparrow}\ \underline{\ \ }\ \underline{\ \ }$ 1 0 -1	$\frac{5}{3}$	1
6 e Ion	$1s^2 2s^2 2p^2$	$^3P_0$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\ \ }$ 1 0 -1	$\frac{5}{3}$	4
7 e Ion	$1s^2 2s^2 2p^3$	$^4S^0_{3/2}$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{5}{3}$	6

8 e Ion	$1s^2 2s^2 2p^4$	$^3P_2$	$\underline{\uparrow\downarrow}_{1}\ \underline{\uparrow}_{0}\ \underline{\uparrow}_{-1}$	$\frac{5}{3}$	6
9 e Ion	$1s^2 2s^2 2p^5$	$^2P^0_{3/2}$	$\underline{\uparrow\downarrow}_{1}\ \underline{\uparrow\downarrow}_{0}\ \underline{\uparrow}_{-1}$	$\frac{5}{3}$	9
10 e Ion	$1s^2 2s^2 2p^6$	$^1S_0$	$\underline{\uparrow\downarrow}_{1}\ \underline{\uparrow\downarrow}_{0}\ \underline{\uparrow\downarrow}_{-1}$	$\frac{5}{3}$	12

156. The system of claim 155, wherein the ionization energy for the boron atom is given by

$$E(ionization;\ B) = \frac{(Z-4)e^2}{8\pi\varepsilon_o r_5} + \Delta E_{mag}$$
$$= 8.147170901\ eV + 0.15548501\ eV = 8.30265592\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

157. The system of claim 156, wherein the ionization energies for the n-electron atoms having the radii, r_n ,are given by the negative of the electric energy, $E(electric)$, given by

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}.$$

158. The system of claim 157, wherein the radii of the 3p electrons are given using the forces given by

$$\mathbf{F}_{ele} = \frac{(Z-n)e^2}{4\pi\varepsilon_o r_n^2}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{diamagnetic} = -\left(\frac{2}{3}+\frac{2}{3}+\frac{1}{3}\right)\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = -\left(\frac{5}{3}\right)\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\,2} = \frac{1}{Z}\frac{8\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

and the radii r_{12} are given by

$$r_{12} = \frac{\dfrac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)} \pm a_0\sqrt{\left(\dfrac{1}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}}}{2}$$

r_{10} *in units of* a_0

159. The system of claim 158, wherein the ionization energies are given by electric energy given by:

$$E(Ionization) = -Electric\ Energy = \frac{(Z-(n-1))e^2}{8\pi\varepsilon_o r_n}.$$

160. The system of claim 159, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration $1s^2 2s^2 2p^6 3s^2 3p^{n-12}$, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by:

$$r_1 = r_2 = a_o \left[\frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right]$$

two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by:

$$r_4 = r_3 = \frac{\left(\frac{a_0 \left(1 - \frac{\sqrt{\frac{3}{4}}}{Z} \right)}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)} \pm a_o \sqrt{\frac{\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z} \right)^2}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)^2} + 4 \frac{\left[\frac{Z-3}{Z-2} \right] r_1 10 \sqrt{\frac{3}{4}}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)}} \right)}{2}$$

r_1 *in units of* a_o

three sets of paired indistinguishable electrons in an orbitsphere with radius r_{10} given by:

$$r_{10} = \frac{\frac{a_0}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)} \right)^2 + \frac{20\sqrt{3} \left(\left[\frac{Z-10}{Z-9} \right] \left(1 - \frac{\sqrt{2}}{2} \right) r_3 \right)}{\left((Z-9) - \left(\frac{5}{24} - \frac{6}{Z} \right) \frac{\sqrt{3}}{r_3} \right)}}}{2}$$

r_3 *in units of* a_0

two indistinguishable spin-paired electrons in an orbitsphere with radius r_{12} given by:

$$r_{12} = \frac{\frac{a_0}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-12}{Z-11}\right]\left(1+\frac{\sqrt{2}}{2}\right)r_{10}\right)}{\left((Z-11)-\left(\frac{1}{8}-\frac{3}{Z}\right)\frac{\sqrt{3}}{r_{10}}\right)}}}{2}$$

r_{10} *in units of* a_0

and $n-12$ electrons in a 3p orbitsphere with radius r_n given by

$$r_n = \frac{\frac{a_0}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)} \pm a_0 \sqrt{\left(\frac{1}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{Z-n}{Z-(n-1)}\right]\left(1-\frac{\sqrt{2}}{2}+\frac{1}{2}\right)r_{12}\right)}{\left((Z-(n-1))-\left(\frac{A}{8}-\frac{B}{2Z}\right)\frac{\sqrt{3}}{r_{12}}\right)}}}{2}$$

r_{12} *in units of* a_0

where the positive root must be taken in order that $r_n > 0$;

the parameter A corresponds to the diamagnetic force, $\mathbf{F}_{diamagnetic}$:

$\mathbf{F}_{diamagnetic} = -\sum_m \frac{(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}\frac{\hbar^2}{4m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$, and the parameter B corresponds to the paramagnetic force, $\mathbf{F}_{mag\ 2}$:

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = (4+4+4)\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r = \frac{1}{Z}\frac{12\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{4\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r, \text{ and}$$

$$\mathbf{F}_{mag\ 2} = \frac{1}{Z}\frac{8\hbar^2}{m_e r_n^2 r_{12}}\sqrt{s(s+1)}\mathbf{i}_r,$$

wherein the parameters of thirteen to eighteen-electron atoms are

Atom Type	Electron Configuration	Ground State Term	Orbital Arrangement of 3p Electrons (3p state)	Diamagnetic Force Factor *A*	Paramagnetic Force Factor *B*
Neutral 13 e Atom *Al*	$1s^2 2s^2 2p^6 3s^2 3p^1$	$^2P^0_{1/2}$	$\underline{\uparrow}\ \underline{\ }\ \underline{\ }$ 1 0 -1	$\frac{11}{3}$	0
Neutral 14 e Atom *Si*	$1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_0$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\ }$ 1 0 -1	$\frac{7}{3}$	0
Neutral 15 e Atom *P*	$1s^2 2s^2 2p^6 3s^2 3p^3$	$^4S^0_{3/2}$	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{5}{3}$	2
Neutral 16 e Atom *S*	$1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_2$	$\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{4}{3}$	1
Neutral 17 e Atom *Cl*	$1s^2 2s^2 2p^6 3s^2 3p^5$	$^2P^0_{3/2}$	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}$ 1 0 -1	$\frac{2}{3}$	2
Neutral 18 e Atom *Ar*	$1s^2 2s^2 2p^6 3s^2 3p^6$	$^1S_0$	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$ 1 0 -1	$\frac{1}{3}$	4
13 e Ion	$1s^2 2s^2 2p^6 3s^2 3p^1$	$^2P^0_{1/2}$	$\underline{\uparrow}\ \underline{\ }\ \underline{\ }$ 1 0 -1	$\frac{5}{3}$	12

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14 e Ion $1s^2 2s^2 2p^6 3s^2 3p^2$	$^3P_0$	$\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\quad}$	$\frac{1}{3}$		
		1 0 -1		16	
15 e Ion $1s^2 2s^2 2p^6 3s^2 3p^3$	$^4S^0_{3/2}$	$\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$			
		1 0 -1	0	24	
16 e Ion $1s^2 2s^2 2p^6 3s^2 3p^4$	$^3P_2$	$\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$	$\frac{1}{3}$		
		1 0 -1		24	
17 e Ion $1s^2 2s^2 2p^6 3s^2 3p^5$	$^2P^0_{3/2}$	$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow}$	$\frac{2}{3}$		
		1 0 -1		32	
18 e Ion $1s^2 2s^2 2p^6 3s^2 3p^6$	$^1S_0$	$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$			
		1 0 -1	0	40	

161. The system of claim 160 wherein the bond comprises a H_2-type MO with two paired electron wherein the formation of the H_2-type MO by the contribution of an electron from each participating atom results in a diamagnetic force between the remaining atomic electrons and the H_2-type MO which causes the H_2-type MO to move to greater principal axes than would result with the Coulombic force alone.

162. The system of claim 161 wherein the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining atomic electrons of each atom decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms.

163. The system of claim 162 wherein the general equation for the central Coulomb force on the outer-most shell (nth where $n = Z - 1$) electron due to the nucleus and the inner electrons is given by:

$$\mathbf{F}_{ele} = \frac{2e^2}{4\pi\varepsilon_0 r_n^2}\mathbf{i}_r$$

for $r > r_{n-1}$.

164. The system of claim 163 wherein the general equation for $\mathbf{F}_{diamagnetic}$ due to the p-orbital contribution is given by

$$\mathbf{F}_{diamagnetic} = -A\frac{\hbar^2}{12m_e r_n^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r$$

165. The system of claim 164 wherein the general equation for $\mathbf{F}_{mag\ 2}$ is given by

$$\mathbf{F}_{mag\ 2} = B\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

166. The system of claim 165 wherein the general equation for $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +1 outside of its radius is given by

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{1}{2}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r$$

167. The system of claim 166 wherein the general equation for $\mathbf{F}_{mag\ 3}$, due to the contribution of a $2p$ electron from each binding atom in the formation of the σ MO that gives rise to a paramagnetic force on the remaining two $2p$ electrons that pair, is given by

$$\mathbf{F}_{mag\ 3} = C\frac{\hbar^2}{4m_e r_n^3}\sqrt{s(s+1)}\mathbf{i}_r$$

168. The system of claim 167 wherein the parameters A, B, and C are zero or a positive integer such that the resulting energy of the molecule is minimized and the electron angular momentum is conserved in the formation of the specie.

169. The system of claim 168 wherein the radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic and paramagnetic forces:

$$\frac{m_e v_n^2}{r_n} = \left(\begin{array}{l} \frac{2e^2}{4\pi\varepsilon_0 r_n^2} - A\frac{\hbar^2}{12 m_e r_n^2 r_3}\sqrt{s(s+1)} + B\frac{\hbar^2}{Z m_e r_n^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{1}{2}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_n^4 m_e}10\sqrt{s(s+1)} + C\frac{\hbar^2}{4 m_e r_n^3}\sqrt{s(s+1)} \end{array} \right)$$

170. The system of claim 169 wherein the radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic and paramagnetic forces where the velocity given by $v_n = \frac{\hbar}{m_e r_n}$ and $s = \frac{1}{2}$ gives:

$$\frac{\hbar^2}{m_e r_n^3} - C\frac{\hbar^2}{4 m_e r_n^3}\sqrt{\frac{3}{4}} = \frac{2e^2}{4\pi\varepsilon_0 r_n^2} - A\frac{\hbar^2}{12 m_e r_n^2 r_3}\sqrt{\frac{3}{4}} + B\frac{\hbar^2}{Z m_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{1}{2}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_n^4 m_e}10\sqrt{\frac{3}{4}}$$

171. The system of claim 170 wherein the general equation for the radius of the shell of the remaining electrons is given by

$$r_6 = \frac{\frac{a_0\left(1-C\frac{\sqrt{3}}{8}\right)}{\left(2-\left(\frac{A}{12}-\frac{B}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0\sqrt{\left(\frac{1-C\frac{\sqrt{3}}{8}}{\left(2-\left(\frac{A}{12}-\frac{B}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \frac{20\sqrt{3}\left(\left[\frac{1}{2}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left(2-\left(\frac{A}{12}-\frac{B}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2}$$

r_3 *in units of* a_0

172. The system of claim 171 wherein the radii r_3 are given by

$$r_4 = r_3 = \frac{\left(\frac{a_0\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)} \pm a_o \sqrt{\frac{\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2} + 4\frac{\left[\frac{Z-3}{Z-2}\right] r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}} \right)}{2}$$

r_1 *in units of* a_o

173. The system of claim 172, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration $1s^2 2s^2 2p^{n-4}$, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by:

$$r_1 = r_2 = a_o\left[\frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)}\right];$$

and two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by:

$$r_4 = r_3 = \frac{\left(a_0\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right) \Big/ \left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right) \pm a_o \sqrt{\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)^2 \Big/ \left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2 + 4\frac{\left[\frac{Z-3}{Z-2}\right] r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}} \right)}{2}$$

r_1 *in units of* a_o

174. The system of claim 173 wherein the sum $E_T\left(molecule, AOs\right)$ of the Coulombic energy change of the AO electrons of both atoms of a bond is given by using the initial radius r_n of each atom and the final radius r_{n-1} of the binding shell of each atom and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell:

$$E_T\left(molecule, AOs\right) = \sum_{m=n_1-3}^{n_1-2} \frac{(Z-m)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_{n_1-1}}-\frac{1}{r_{n_1}}\right) + \sum_{m=n_2-3}^{n_2-2} \frac{(Z-m)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_{n_2-1}}-\frac{1}{r_{n_2}}\right)$$

where the subscript designates atom 1 and atom 2 of the bond.

175. The system of claim 174 wherein the forces on the electrons of the MO are the Coulombic force:

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_\xi ;$$

the spin pairing force:

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi$$

the diamagnetic force:

$$\mathbf{F}_{diamagneticMO1} = -\frac{n_e \hbar^2}{4m_e a^2 b^2} D\mathbf{i}_\xi$$

where n_e is the total number of electrons that interact with the binding σ-MO electron, the force on the pairing electron of the σ MO:

$$\mathbf{F}_{diamagneticMO2} = -\frac{1}{Z}\frac{|L|\hbar}{2m_e a^2 b^2} D\mathbf{i}_\xi$$

where $|L|$ is the magnitude of the angular momentum of each atom at a focus that is the source of the diamagnetism at the σ-MO, and the centrifugal force:

$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi$$, wherein the force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis.

176. The system of claim 175 wherein the force balance equation for the σ-MO with $n_e = 2$ and $|L| = \hbar$ is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \left(2 + \frac{1}{Z}\right) a_0$$

177. The system of claim 176 wherein the force balance equation for the σ-MO with $n_e = 2$ and $|L| = \sqrt{\frac{3}{4}}\hbar$ is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(\frac{3}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right)\frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \left(\frac{5}{2} + \frac{\sqrt{\frac{3}{4}}}{Z}\right) a_0$$

178. The system of claim 177 wherein the force balance equation for the σ-MO $n_e = 2$, and $|L| = \hbar$:

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2 m_e a^2 b^2} D - \left(\frac{5}{2} + \frac{1}{2Z}\right) \frac{\hbar^2}{2 m_e a^2 b^2} D$$

$$a = \left(\frac{7}{2} + \frac{1}{2Z}\right) a_0$$

179. The system of claim 178 wherein the Coulombic force is

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 a b^2} D \mathbf{i}_\xi ;$$

the spin pairing force is

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2 m_e a^2 b^2} D \mathbf{i}_\xi$$

the force on the electrons of the MO due to two paired electrons in at least one shell with $n_e = 2$ is

$$\mathbf{F}_{diamagneticMO1} = -\frac{\hbar^2}{2 m_e a^2 b^2} D \mathbf{i}_\xi ;$$

the force $\mathbf{F}_{diamagneticMO2}$ is given by the sum of the contributions over the components of angular momentum $|L|$ of the atoms at the foci acting on the electrons of the σ-MO:

$$\mathbf{F}_{diamagneticMO2} = -\sum_{i,j} \frac{|L_i| \hbar}{Z_j 2 m_e a^2 b^2} D \mathbf{i}_\xi , \text{ and}$$

the centrifugal force is

$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D \mathbf{i}_\xi .$$

180. The system of claim 179 wherein the force balance equation for the σ-MO of the carbon nitride radical comprising carbon with charge $Z_1 = 6$ and $|L_1| = \hbar$ and $|L_2| = \sqrt{\frac{3}{4}}\hbar$ and nitrogen with $Z_2 = 7$ and $|L_3| = \hbar$ is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) a_0$$

181. The system of claim 180 wherein the Coulombic force is

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_\xi ;$$

the spin pairing force is

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi$$

the force on the electrons of the MO due to two paired electrons in at least one shell with $n_e = 2$ is

$$\mathbf{F}_{diamagneticMO1} = -\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi ;$$

the force $\mathbf{F}_{diamagneticMO2}$ is given by the sum of the contributions over the components of angular momentum $|L|$ of the atoms at the foci acting on the electrons of the σ-MO:

$$\mathbf{F}_{diamagneticMO2} = -\sum_{i,j} \frac{|L_i|\hbar}{Z_j 2m_e a^2 b^2} D\mathbf{i}_\xi , \text{ and}$$

the centrifugal force is

$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi .$$

182. The system of claim 181 wherein the force balance equation for the σ-MO of the carbon nitride radical comprising carbon with charge $Z_1 = 6$ and $|L_1| = \hbar$ and $|L_2| = \sqrt{\frac{3}{4}}\hbar$ and nitrogen with $Z_2 = 7$ and $|L_3| = \hbar$ is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{1}{Z_2}\right) a_0$$

183. The system of claim 182 wherein the Coulombic force is

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 a b^2} D\mathbf{i}_\xi ;$$

the spin pairing force is

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi$$

the force on the electrons of the MO due to two paired electrons in at least one shell with $n_e = 2$ is

$$\mathbf{F}_{diamagneticMO1} = -\frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi ;$$

the force $\mathbf{F}_{diamagneticMO2}$ is given by the sum of the contributions over the components of angular momentum $|L|$ of the atoms at the foci acting on the electrons of the σ-MO, and the sum of the contributions from atom 1 with $Z = Z_1$ and atom 2 with $Z = Z_2$ with $|L_i| = \hbar$ is

$$\mathbf{F}_{diamagneticMO2} = -\left(\frac{1}{Z_1} + \frac{1}{Z_2}\right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi , \text{ and}$$

the centrifugal force is

$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi .$$

184. The system of claim 183 wherein force balance equation for the σ-MO of the carbon monoxide molecule is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 a b^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \left(\frac{1}{Z_1} + \frac{1}{Z_2}\right)\right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a=\left(2+\frac{1}{Z_1}+\frac{1}{Z_2}\right)a_0$$

185. The system of claim 184 wherein the Coulombic force is

$$\mathbf{F}_{Coulomb}=\frac{e^2}{8\pi\varepsilon_0 ab^2}D\mathbf{i}_\xi;$$

the spin pairing force is

$$\mathbf{F}_{spin-pairing}=\frac{\hbar^2}{2m_e a^2 b^2}D\mathbf{i}_\xi$$

the force on the electrons of the MO due to two paired electrons in at least one shell with $n_e=2$ is

$$\mathbf{F}_{diamagneticMO1}=-\frac{\hbar^2}{2m_e a^2 b^2}D\mathbf{i}_\xi;$$

the force $\mathbf{F}_{diamagneticMO2}$ of the nitric oxide radical comprising nitrogen with charge $Z_1=7$ and $|L_1|=\hbar$ and $|L_2|=\sqrt{\frac{3}{4}}\hbar$ and oxygen with $Z_2=8$ and $|L_3|=\hbar$ given by the corresponding sum of the contributions is

$$\mathbf{F}_{diamagneticMO2}=-\left(\frac{1}{Z_1}+\frac{\sqrt{\frac{3}{4}}}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2}D\mathbf{i}_\xi, \text{ and}$$

the centrifugal force is

$$\mathbf{F}_{centrifugalMO}=-\frac{\hbar^2}{m_e a^2 b^2}D\mathbf{i}_\xi.$$

186. The system of claim 185 wherein the general force balance equation for the σ-MO of the nitric oxide radical is the same as that of CN:

$$\frac{\hbar^2}{m_e a^2 b^2}D=\frac{e^2}{8\pi\varepsilon_0 ab^2}D+\frac{\hbar^2}{2m_e a^2 b^2}D-\left(1+\frac{1}{Z_1}+\frac{\sqrt{\frac{3}{4}}}{Z_1}+\frac{1}{Z_2}\right)\frac{\hbar^2}{2m_e a^2 b^2}D$$

$$a=\left(2+\frac{1}{Z_1}+\frac{\sqrt{\frac{3}{4}}}{Z_1}+\frac{1}{Z_2}\right)a_0$$

where $Z_1=7$ and $Z_2=8$ for NO and $Z_1=6$ and $Z_2=7$ for CN.

187. The system of claims 186 and 63 wherein the distance from the origin of the H_2-type-ellipsoidal-MO to each focus c', the internuclear distance $2c'$, and the length of the semiminor axis of the prolate spheroidal H_2-type MO $b=c$ are solved from the semimajor axis a.

188. The system of claim 187 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e=n_1c_1c_2\frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}};$$

The potential energy of the two nuclei is

$$V_p=n_1\frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}};$$

The kinetic energy of the electrons is

$$T=n_1c_1c_2\frac{\hbar^2}{2m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}},\text{ and}$$

The energy, V_m, of the magnetic force between the electrons is

$$V_m=n_1c_1c_2\frac{-\hbar^2}{4m_ea\sqrt{a^2-b^2}}\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}},\text{ and}$$

the total energy, E_T, is given by the sum of the energy terms plus $E(AO)$:

$$E_T=V_e+T+V_m+V_p$$

$$E_T=-\frac{n_1e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]$$

$$=-\frac{n_1e^2}{8\pi\varepsilon_0c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and $E(AO)$ is the energy of the at least one atomic orbital to which the MO is energy matched.

189. The system of claim 188 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$, and

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}.$$

190. The system of claim 189 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{ -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2 - \frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_1 c_2 e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right] - n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

where R is b or a, n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and $E(AO)$ is the energy of the at least one atomic orbital to which the MO is energy matched.

191. The system of claim 190 wherein the bond comprises a H_2-type MO with four paired electron wherein the formation of the H_2-type MO by the contribution of two electrons from each participating atom results in a diamagnetic force between the remaining atomic electrons and the H_2-type MO which causes the H_2-type MO to move to greater principal axes than would result with the Coulombic force alone.

192. The system of claim 191 wherein the integer increase of the central field and the resulting increased Coulombic as well as magnetic central forces on the remaining atomic electrons of each atom decrease the radius of the corresponding shell such that the energy minimum is achieved that is lower than that of the reactant atoms.

193. The system of claim 192 wherein the general equation for the central Coulomb force on the outer-most shell (nth where $n = Z - 2$) electron due to the nucleus and the inner electrons is given by:

$$\mathbf{F}_{ele} = \frac{3e^2}{4\pi\varepsilon_0 r_n^2}\mathbf{i}_r$$

for $r > r_{n-1}$.

194. The system of claim 193 wherein the general equation for $\mathbf{F}_{diamagnetic}$ due to the p-orbital contribution is given by

$$\mathbf{F}_{diamagnetic} = -A\frac{\hbar^2}{12 m_e r_n^2 r_3}\sqrt{\frac{3}{4}}\mathbf{i}_r$$

195. The system of claim 194 wherein the general equation for $\mathbf{F}_{mag\ 2}$ is given by

$$\mathbf{F}_{mag\ 2} = B\frac{1}{Z}\frac{\hbar^2}{m_e r_n^2 r_3}\sqrt{s(s+1)}\mathbf{i}_r$$

196. The system of claim 195 wherein the general equation for $\mathbf{F}_{diamagnetic\ 2}$ due to the binding of the p-orbital electron having an electric field of +2 outside of its radius is given by

$$\mathbf{F}_{diamagnetic\ 2} = -\left[\frac{2}{3}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{m_e r_n^4}10\sqrt{s(s+1)}\mathbf{i}_r$$

197. The system of claim 196 wherein the general equation for $\mathbf{F}_{mag\ 3}$, due to the contribution of a $2p$ electron from each binding atom in the formation of the σ MO that gives rise to a paramagnetic force on the remaining two $2p$ electrons that pair, is given by

$$\mathbf{F}_{mag\ 3} = C\frac{\hbar^2}{4m_e r_n^3}\sqrt{s(s+1)}\mathbf{i}_r$$

198. The system of claim 197 wherein the parameters A, B, and C are zero or a positive integer such that the resulting energy of the molecule is minimized and the electron angular momentum is conserved in the formation of the specie.

199. The system of claim 198 wherein the radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic and paramagnetic forces:

$$\frac{m_e v_n^2}{r_n} = \left(\begin{array}{l}\frac{3e^2}{4\pi\varepsilon_0 r_n^2} - A\frac{\hbar^2}{12m_e r_n^2 r_3}\sqrt{s(s+1)} + B\frac{\hbar^2}{Zm_e r_n^2 r_3}\sqrt{s(s+1)} \\ -\left[\frac{2}{3}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_n^4 m_e}10\sqrt{s(s+1)} + C\frac{\hbar^2}{4m_e r_n^3}\sqrt{s(s+1)}\end{array}\right) \quad (13.626)$$

200. The system of claim 199 wherein the radius of the $2p$ shell is calculated by equating the outward centrifugal force to the sum of the electric and diamagnetic and paramagnetic forces where the velocity given by $v_n = \frac{\hbar}{m_e r_n}$ and $s = \frac{1}{2}$ gives:

$$\frac{\hbar^2}{m_e r_n^3} - C\frac{\hbar^2}{4m_e r_n^3}\sqrt{\frac{3}{4}} = \frac{3e^2}{4\pi\varepsilon_0 r_n^2} - A\frac{\hbar^2}{12m_e r_n^2 r_3}\sqrt{\frac{3}{4}} + B\frac{\hbar^2}{Zm_e r_6^2 r_3}\sqrt{\frac{3}{4}} - \left[\frac{2}{3}\right]\left(1-\frac{\sqrt{2}}{2}\right)\frac{r_3\hbar^2}{r_n^4 m_e}10\sqrt{\frac{3}{4}}$$

201. The system of claim 200 wherein the general equation for the radius of the shell of the remaining electrons is given by

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$$r_6 = \frac{\dfrac{a_0\left(1-C\frac{\sqrt{3}}{8}\right)}{\left(3-\left(\frac{A}{12}-\frac{B}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)} \pm a_0 \sqrt{\left(\dfrac{1-C\frac{\sqrt{3}}{8}}{\left(3-\left(\frac{A}{12}-\frac{B}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}\right)^2 + \dfrac{20\sqrt{3}\left(\left[\frac{2}{3}\right]\left(1-\frac{\sqrt{2}}{2}\right)r_3\right)}{\left(3-\left(\frac{A}{12}-\frac{B}{Z}\right)\frac{\sqrt{3}}{2r_3}\right)}}}{2}$$

r_3 *in units of* a_0

202. The system of claim 201 wherein the radii r_3 are given by

$$r_4 = r_3 = \frac{\left(\dfrac{a_0\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)} \pm a_o \sqrt{\dfrac{\left(1-\frac{\sqrt{\frac{3}{4}}}{Z}\right)^2}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)^2} + 4\dfrac{\left[\frac{Z-3}{Z-2}\right]r_1 10\sqrt{\frac{3}{4}}}{\left((Z-3)-\left(\frac{1}{4}-\frac{1}{Z}\right)\frac{\sqrt{\frac{3}{4}}}{r_1}\right)}}\right)}{2}$$

r_1 *in units of* a_o

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203. The system of claim 202, wherein for each n-electron atom having a central charge of Z times that of the proton and an electron configuration $1s^2 2s^2 2p^{n-4}$, there are two indistinguishable spin-paired electrons in an orbitsphere with radii r_1 and r_2 both given by:

$$r_1 = r_2 = a_o \left[\frac{1}{Z-1} - \frac{\sqrt{\frac{3}{4}}}{Z(Z-1)} \right];$$

and two indistinguishable spin-paired electrons in an orbitsphere with radii r_3 and r_4 both given by:

$$r_4 = r_3 = \frac{\left(\frac{a_0 \left(1 - \frac{\sqrt{\frac{3}{4}}}{Z} \right)}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)} \pm a_o \sqrt{\frac{\left(1 - \frac{\sqrt{\frac{3}{4}}}{Z} \right)^2}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)^2} + 4 \frac{\left[\frac{Z-3}{Z-2} \right] r_1 10 \sqrt{\frac{3}{4}}}{\left((Z-3) - \left(\frac{1}{4} - \frac{1}{Z} \right) \frac{\sqrt{\frac{3}{4}}}{r_1} \right)}} \right)}{2}$$

r_1 *in units of* a_o

204. The system of claim 203 wherein the force balance of a double-bond MO corresponds to that of a second pair of two electrons binding to a molecular ion having $+2e$ at each focus and a first bound pair such that the forces are the same as those of a molecule ion having $+e$ at each focus.

205. The system of claim 204 wherein the forces on the electrons of the MO are the Coulombic force:

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_\xi;$$

the spin pairing force:

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi ;$$

the diamagnetic force:

$$\mathbf{F}_{diamagneticMO1} = -\frac{n_e \hbar^2}{4m_e a^2 b^2} D\mathbf{i}_\xi$$

where n_e is the total number of electrons that interact with the binding σ-MO electron;

the force on the pairing electron of the σ MO:

$$\mathbf{F}_{diamagneticMO2} = -\frac{1}{Z}\frac{|L|\hbar}{2m_e a^2 b^2} D\mathbf{i}_\xi$$

where $|L|$ is the magnitude of the angular momentum of each atom at a focus that is the source of the diamagnetism at the σ-MO, and

the centrifugal force:

$$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi , \text{ and}$$

the force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis.

206. The system of claim 205 wherein the forces on the electrons of the NO_2 MO are the Coulombic force:

$$\mathbf{F}_{Coulomb} = \frac{e^2}{8\pi\varepsilon_0 ab^2} D\mathbf{i}_\xi ;$$

the spin pairing force:

$$\mathbf{F}_{spin-pairing} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi ;$$

the diamagnetic force $\mathbf{F}_{diamagneticMO1}$ for each σ-MO of the NO_2 molecule due to the two paired electrons in the $O2p$ shell with $n_e = 2$:

$$\mathbf{F}_{diamagneticMO1} = \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi$$

which is also the corresponding force of NO;

$\mathbf{F}_{diamagneticMO2}$ of the nitrogen dioxide molecule comprising nitrogen with charge $Z_1 = 7$

and $|L_1| = \hbar$ and $|L_2| = \sqrt{\frac{3}{4}}\hbar$ and the two oxygen atoms, each with $Z_2 = 8$ and $|L_3| = \hbar$ given by the corresponding sum of the contributions:

$$\mathbf{F}_{diamagneticMO2} = \left(\frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D\mathbf{i}_\xi$$

which is also the corresponding force of NO and CN except the term due to oxygen is twice that of NO due to the two oxygen atoms of NO_2, and

the centrifugal force

$\mathbf{F}_{centrifugalMO} = -\frac{\hbar^2}{m_e a^2 b^2} D\mathbf{i}_\xi$, and

the force balance of the centrifugal force equated to the Coulombic and magnetic forces is solved for the length of the semimajor axis.

207. The system of claim 206 wherein the force balance equation for the σ-MOs of NO_2 with $Z_1 = 7$ and $Z_2 = 8$ is

$$\frac{\hbar^2}{m_e a^2 b^2} D = \frac{e^2}{8\pi\varepsilon_0 ab^2} D + \frac{\hbar^2}{2m_e a^2 b^2} D - \left(1 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) \frac{\hbar^2}{2m_e a^2 b^2} D$$

$$a = \left(2 + \frac{1}{Z_1} + \frac{\sqrt{\frac{3}{4}}}{Z_1} + \frac{2}{Z_2} \right) a_0$$

208. The system of claims 207 and 63 wherein the distance from the origin of the H_2-type-ellipsoidal-MO to each focus c', the internuclear distance $2c'$, and the length of the semiminor axis of the prolate spheroidal H_2-type MO $b = c$ are solved from the semimajor axis a.

209. The system of claim 208 wherein the sum $E_T(molecule, AOs)$ of the Coulombic energy change of the AO electrons of the participating atoms or ions of the bonds of the specie is the sum of the contributions over all such atoms or ions given by using the initial radius r_n of the atom or ion and the final radius r_{n-2} of the binding shell of the atom or ion and by considering that the central Coulombic field decreases by an integer for each successive electron of the shell:

$$E_T(molecule, AOs) = \sum_{m=n_1-4}^{n_1-3} \frac{(Z-m)e^2}{8\pi\varepsilon_0}\left(\frac{1}{r_{n_1-2}} - \frac{1}{r_{n_1}}\right)$$

where the subscript designates the exemplary atom 1 of the bond.

210. The system of claim 209 wherein the sum $E_T(molecule, AOs)$ of the Coulombic energy change of the AO electron of a participating atom of a bond wherein all of the electrons of the shell of the AO are contributed to the bond is given by the sum of the corresponding ionization energies of the AO electrons.

211. The system of claim 210 wherein energy of the double bond MO is match to the participating AOs and the potential energy of the four electrons in the central field of the nuclei at the foci is

$$V_e = 2^2 n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}};$$

The potential energy of the two nuclei is

$$V_p = 2^2 n_1 \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}};$$

The kinetic energy of the electrons is

$$T = 2n_1 c_1 c_2 \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The energy, V_m, of the magnetic force between the electrons is

$$V_m = 2^2 n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms plus $E(AO)$:

$$E_T = V_e + T + V_m + V_p$$

$$E_T = -\frac{2^2 n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1c_2(2)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+n_1E(AO)$$

$$=-\frac{2^2 n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2(2)\ln\frac{a+c'}{a-c'}-1\right]+n_1E(AO)$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and $E(AO)$ is the energy of the at least one atomic orbital to which the MO is energy matched.

212. The system of claim 211 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$, and

the total energy is

$$E_T = V_e + T + V_m + V_p + E(AO) + \overline{E}_{osc}.$$

213. The system of claim 212 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$E_T = -2^2\frac{n_1e^2}{8\pi\varepsilon_0c'}\left[c_1c_2(2)\ln\frac{a+c'}{a-c'}-1\right]+n_1E(AO)+\overline{E}_{osc}$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond, and $E(AO)$ is the energy of the at least one atomic orbital to which the MO is energy matched.

214. The system of claim 213 wherein the energy components of are V_e, V_p, T, V_m, and E_T, except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to each σ-MO double bond.

215. The system of claim 214 wherein the potential energy of the four electrons of double bond in the central field of the nuclei at the foci is

$$V_e = 2^2 n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}};$$

The potential energy of the two nuclei is

$$V_p = 2^2 n_1 \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}};$$

The kinetic energy of the electrons is

$$T = 2n_1 c_1 c_2 \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The energy, V_m, of the magnetic force between the electrons is

$$V_m = 2^2 n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$E_T = -\frac{2^2 n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1 c_2 (2)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} - 1\right].$$

$$= -\frac{2^2 n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2 (2)\ln\frac{a+c'}{a-c'} - 1\right]$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

216. The system of claim 215 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}, \text{ and}$$

the total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}.$$

217. The system of claim 216 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$E_T = -\frac{2^2 n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2 (2)\ln\frac{a+c'}{a-c'} - 1\right] + \overline{E}_{osc}$$

n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

218. The system of claim 217 wherein the total energy of the specie is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, the change in the energy of the AOs or HOs upon forming the bond, the change in magnetic energy with bond formation, and the energy of oscillation in the transition state.

219. The system of claim 218 wherein the total energy of the specie is the sum over all of the component groups wherein the total energy of each said group is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, the change in the energy of the AOs or HOs upon forming the bond, the change in magnetic energy with bond formation, and the energy of oscillation in the transition state.

220. The system of claim 219 wherein the change in magnetic energy is given by

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r_n^3} = \frac{8\pi\mu_o\mu_B^2}{r_n^3}$$

where r_n^3 is the radius of the atom that reacts to form the bond.

221. The system of claim 220 wherein the bond energy of the molecular or molecular ion is difference in the energy of the total energy of the starting species and the total energy of the specie.

222. The system of claim 221 wherein the bond energy of a specific bond of the molecular or molecular ion is difference in the energy of the sum of the energies of the atoms and any change in energy of any groups formed with the starting atoms and the total energy of the bond of the specie.

223. The system of claim 222 wherein the total energy of a molecule, $E_T(molecule)$, is given by the sum of:

the sum of the energies of the electrons donated to each bond,

the sum of the energies of electrons of at least one other atom donated to the bonds,

the sum over the participating atoms of each AO contribution due to the decrease in radius with the formation of each bond, and

the σ MO energy contribution per bond.

224. The system of claim 223 wherein the total energy of a molecule, $E_T(molecule)$, is given by the sum of:

the sum of the energies of the electrons donated to each bond such that all of the electrons of the shell are donated,

the sum of the energies of electrons of at least one other atom donated to the bonds,

the sum over the participating atoms of each AO contribution due to the decrease in radius with the formation of each bond, and

the σ MO energy contribution per bond.

225. The system of claim 223 wherein the total energy of CO_2, $E_T(CO_2)$, is given by the sum of $E(ionization;\ C)$ and $E(ionization;\ C^+)$, the sum of the energies of the first and second electrons of carbon donated to each double bond, the sum of $E(ionization;\ O)$ and two times $E(ionization;\ O^+)$, the energies of the first and second electrons of oxygen donated to the double bonds, two times $E_T(O,2p)$, the $O2p$ AO contribution due to the decrease in radius with the formation of each bond and two times $E_T(C=O,\sigma)$, the σ MO contribution:

$$E_T(CO_2) = \begin{pmatrix} E(ionization;\ C) + E(ionization;\ C^+) + E(ionization;\ O) \\ +2E(ionization;\ O^+) + 2E_T(O,2p) + 2E_T(C=O,\sigma) \end{pmatrix}$$

$$= \begin{pmatrix} 11.26030\ eV + 24.38332\ eV + 13.61806\ eV \\ +2(35.11730\ eV) + 2(-32.12759\ eV) \\ -2\left(\frac{4e^2}{8\pi\varepsilon_0\sqrt{\frac{2aa_0}{3}}}\left(\left(\frac{3}{2}\right)\ln\frac{a+\sqrt{\frac{2aa_0}{3}}}{a-\sqrt{\frac{2aa_0}{3}}} - 1\right)\right) \end{pmatrix}$$

$$= \begin{pmatrix} 11.26030\ eV + 24.38332\ eV + 13.61806\ eV \\ +2(35.11730\ eV) + 2(-32.12759\ eV) - 2(55.25423\ eV) \end{pmatrix}$$

$$= -55.26841\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

226. The system of claim 225 wherein the total energy of a molecule, $E_{T+osc}(molecule)$ is given by the sum of $E_T(molecule)$ and $\overline{E}_{osc}$.

227. The system of claim 226 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_{hv}\sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right), \text{ and}$$

where the angular frequency of the reentrant oscillation in the transition state is

$$\omega = \sqrt{\frac{c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3}}{m_e}};$$

the kinetic energy, E_K, is given by Planck's:

$$\overline{E}_K = \hbar\omega = \hbar\sqrt{\frac{c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3}}{m_e}};$$

the Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_D \cong E_{hv}\sqrt{\frac{2\overline{E}_K}{m_e c^2}} = E_{hv}\sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_e c^2}}$$

$\overline{E}_{osc}$ is given by the sum of and $\overline{E}_{Kvib}$, the vibrational energy:

$$\overline{E}_{osc}\left(molecule\right) = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_{hv}\sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_e c^2}} + E_{vib}\right)$$

where R is b or a, n_1 is the number of equivalent bonds of the MO, c_{BO} is the bond-order factor which is 1 for a single bond, 4 for a double bond, and 9 for a triplet bond, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

228. The system of claim 227 wherein E_{hv} is given by $E_T\left(molecule\right)/2$ in the case of a double bond such that

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = E_T(molecule)/2\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}.$$

229. The system of claim 228 wherein $E_{h\nu}$ of a molecule having n_1 bonds is given by $E_T(molecule)/n_1$ such that

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_T(molecule)/n_1\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right).$$

230. The system of claim 229 wherein $E_{h\nu}$ of a molecule having n_1 bonds is given by $E_T(H_2)$ such that

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_T(H_2)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right).$$

where $E_T(H_2) = -31.63537\ eV$ is the total energy of the hydrogen molecule, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

231. The system of claim 230 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_{h\nu}\sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right), \text{ and}$$

where the angular frequency of the reentrant oscillation in the transition state is determined by the force between the central field and the electrons in the transition state; said force and its derivative are given by

$$f(R) = -c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3}$$

and

$$f'(a) = 2c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3}$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a} f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO} \frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3}}{m_e}}$$

where R is b or a, c_{BO} is the bond-order factor which is 1 for a single bond, 4 for a double bond, and 9 for a triplet bond, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

232. The system of claim 231 wherein the nucleus of the B atom and the nucleus of the A atom comprise the foci of each H_2-type ellipsoidal MO of the $A-B$ bond and the parameters of the point of intersection of each H_2-type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r = r_0 \frac{1+e}{1+e\cos\theta'}$$

233. The system of claim 232 wherein the radius of the A shell is r_A, and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_A = (a-c') \frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'}, \text{ and}$$

the polar angle θ' at the intersection point is given by

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{a_0} - 1\right)\right)$$

234. The system of claim 233 wherein the angle $\theta_{A\,AO}$ the radial vector of the A AO makes with the internuclear axis is

$$\theta_{A\,AO} = 180° - \theta'$$

235. The system of claim 234 wherein the distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A \sin\theta_{A\,AO} = b \sin\theta_{H_2MO}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{r_a \sin\theta_{A\,AO}}{b};$$

the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$d_{H_2MO} = a\cos\theta_{H_2MO}$, and

the distance $d_{A\,AO}$ along the internuclear axis from the origin of the A atom to the point of intersection of the orbitals is given by

$$d_{A\,AO} = c' - d_{H_2MO}.$$

236. The system of claim 235 where the bond angle is determined from the zero energy condition of the total energy of the potential bond between any pair of terminal atoms.

237. The system of claim 236 where the force constant k' of a H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{c_1 c_2 2e^2}{4\pi\varepsilon_o}$$

where c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie and c_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond.

238. The system of claim 237 where the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2k' a}} = \sqrt{\frac{aa_0}{2k'}};$$

the internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2k'}};$$

the length of the semiminor axis of the prolate spheroidal MO $b = c$ is given by

$b = \sqrt{a^2 - c'^2}$, and

and, the eccentricity, e, is

$$e = \frac{c'}{a}.$$

239. The system of claim 238 wherein the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}};$$

The potential energy of the two nuclei is

$$V_p = \frac{e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}};$$

The kinetic energy of the electrons is

$$T = c_1 c_2 \frac{\hbar^2}{2m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}, \text{ and}$$

The energy, V_m, of the magnetic force between the electrons is

$$V_m = c_1 c_2 \frac{-\hbar^2}{4m_e a\sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}, \text{ and}$$

The total energy, E_T, is given by the sum of the energy terms:

$$E_T = V_e + T + V_m + V_p$$

$$E_T = -\frac{e^2}{8\pi\varepsilon_o \sqrt{a^2 - b^2}} \left[c_1 c_2 \left(2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right].$$

$$= -\frac{e^2}{8\pi\varepsilon_0 c'} \left[c_1 c_2 \left(2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right]$$

where c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

240. The system of claim 239 wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the difference between the Doppler and average vibrational kinetic energies:

$$\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib} = \left(V_e + T + V_m + V_p\right)\sqrt{\frac{2\overline{E}_K}{Mc^2}} + n_1 \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}, \text{ and}$$

The total energy is

$$E_T = V_e + T + V_m + V_p + \overline{E}_{osc}$$

$$E_T = -\left\{\frac{e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2 - \frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right]\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_1 c_2 e^2}{4\pi\varepsilon_o a^3}}}{m_e c^2}}\right] - \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right\}$$

where c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

241. The system of claim 240 wherein the vibrational energy $\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$ is given by

$$+\frac{1}{2}\hbar\sqrt{\frac{\frac{c_1 e^2}{8\pi\varepsilon_o a^3} - \frac{e^2}{8\pi\varepsilon_o (a+c')^3}}{\mu}}$$

where μ is the reduced mass of the nuclei.

242. The system of claim 241 wherein the energy components of are V_e, V_p, T, V_m, and E_T, except that the terms based on charge are multiplied by four and the kinetic energy term is multiplied by two due to a σ-MO double bond.

243. The system of claim 242 wherein $c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2k' a}} = \sqrt{\frac{aa_0}{2k'}}$ is substituted into the equation for E_T which is set equal to zero, and the semimajor axis is solved.

244. The system of claims 243 and 63 wherein the distance from the origin of the H_2-type-ellipsoidal-MO to each focus c', the internuclear distance $2c'$, and the length of the semiminor axis of the prolate spheroidal H_2-type MO $b = c$ are solved from the semimajor axis a.

245. The system of claim 244 wherein with $2c'_{A-B}$ defined as the internuclear distance of each $A-B$ bond and $C = 2c'_{B-B}$ defined as the internuclear distance of the two terminal B atoms, the bond angle between the $A-B$ bonds is given by the law of cosines is

$$\theta = \cos^{-1}\left(\frac{2\left(2c'_{A-B}\right)^2 - \left(2c'_{B-B}\right)^2}{2\left(2c'_{A-B}\right)^2}\right)$$

246. The system of claim 245 wherein the specie comprises more than two bonds with one $A-B$ bound along an axis defined as the vertical or z-axis and any two $A-B$ bonds form an isosceles triangle; the angle of the bonds from the defined axis is determined from the geometrical relationships:

the distance $d_{origin-B}$ from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60°};$$

the height along the z-axis from the origin to A nucleus d_{height} is given by

$$d_{height} = \sqrt{\left(2c'_{A-B}\right)^2 - \left(d_{origin-B}\right)^2}\text{, and}$$

the angle θ_v of each $A-B$ bond from the z-axis is given by

$$\theta_v = \tan^{-1}\left(\frac{d_{origin-B}}{d_{height}}\right).$$

247. The system of claim 246 wherein the vibrational energies are determined by the forces between the central field and the electrons and those between the nuclei; said electron-central-field force and its derivative are given by

$$f(R) = -c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3}$$

and

$$f'(a) = 2c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3};$$

said nuclear repulsion force and its derivative are given by

$$f(2c') = \frac{e^2}{8\pi\varepsilon_0 (2c')^2}$$

and

$$f'(2c') = -\frac{e^2}{4\pi\varepsilon_0 (2c')^3}$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{c_1 c_2 e^2}{4\pi\varepsilon_0 R^3} - \frac{e^2}{8\pi\varepsilon_0 (2c')^2}}{\mu}}$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the nuclei, R is b or a, c_{BO} is the bond-order factor which is 1 for a single bond, 4 for a double bond, and 9 for a triplet bond, c_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie, and c_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of each chemical bond.

248. The system of claim 247 wherein the transition-state vibrational energy, $E_{vib}(0)$, given by Planck's equation is:

$$E_{vib}(0) = \hbar\omega$$

249. The system of claim 248 wherein the energy $\tilde{\nu}_\upsilon$ of state υ is given by

$$\tilde{\nu}_\upsilon = \upsilon\omega_0 - \upsilon(\upsilon - 1)\omega_0 x_0, \quad \upsilon = 0,1,2,3...$$

where

$$\omega_0 x_0 = \frac{hc\omega_0^2}{4D_0}$$

ω_0 is the frequency of the $\upsilon = 1 \rightarrow \upsilon = 0$ transition, and D_0 is the bond dissociation energy.

250. The system of claim 249 wherein ω_0 is given by

$$\omega_0 = E_{vib}(0) - 2\omega_0 x_0, \text{ and}$$

$$\omega_0 = E_{vib}(0) - 2\frac{hc\omega_0^2}{4D_0}$$

such that

$$\omega_0^2 + \frac{2D_0}{hc}\omega_0 - \frac{2D_0}{hc}E_{vib}(0) = 0, \text{ and}$$

$$\omega_0 = \frac{-\frac{2D_0}{hc} \pm \sqrt{\left(\frac{2D_0}{hc}\right)^2 + 4\frac{2D_0}{hc}E_{vib}(0)}}{2}.$$

251. The system of claim 250 wherein B_e, the rotational parameter, for $A-B$ is given by:

$$B_e = \frac{\hbar^2}{2I_e hc}$$

where $I = \mu r^2$, $r = 2c'$, and μ is the reduced mass.

252. The system of claim 251 wherein the vibrational energy levels of the $A-A$ and $A-B$ bonds of the specie are solved as sets of coupled atomic harmonic oscillators wherein each atom of a chain of bonds is further coupled to at least one additional harmonic oscillators by using the Lagrangian, the differential equation of motion, and the eigenvalue solutions wherein the spring constants are derived from the central forces.

253. The system of claim 252 wherein the vibrational energy levels of the $C-C$ bonds of C_nH_{2n+2} are solved as $n-1$ sets of coupled carbon harmonic oscillators wherein each carbon is further coupled to two or three equivalent H harmonic oscillators by using the Lagrangian, the differential equation of motion, and the eigenvalue solutions wherein the spring constants are derived from the central forces.

254. The system of claim 253 wherein $E_D(C_nH_{2n+2})$, the total bond dissociation energy of C_nH_{2n+2}, is given as the sum of the energy components due to the two methyl groups, $n-2$ methylene groups, and $n-1$ $C-C$ bonds.

255. The system of claim 254 wherein the total bond dissociation energy of C_nH_{2n+2} is given by

$$E_D(C_nH_{2n+2}) = E_D(C-C)_{n-1} + 2E_{D_{alkane}}\left({}^{12}CH_3\right) + (n-2)E_{D_{alkane}}\left({}^{12}CH_2\right)$$
$$= (n-1)(4.32754\ eV) + 2(12.49186\ eV) + (n-2)(7.83016\ eV)$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

256. The system of claim 255 wherein the exact solution for the dimensional parameters, charge density functions, and energies of molecules are determined using the results for the determination of C_nH_{2n+2} and the functional groups as basis sets that are linearly combined.

257. The system of claim 256 wherein one or more of the hydrogen atoms of the solution for C_nH_{2n+2} are substituted with one or more of the previously solved functional groups or derivative functional groups to give the parameters of a desired molecule.

258. The system of claim 257 wherein the parameters of a given molecule are given by energy matching each group to C_nH_{2n+2}.

259. The system of claim 258 wherein substitution of one or more H's of C_nH_{2n+2} with functional groups from the list of CH_3, other C_nH_{2n+2} groups, $H_2C=CH_2$, $HC\equiv CH$, F, Cl, O, OH, NH, NH_2, CN, NO, NO_2, CO, CO_2, and C_6H_6 give the solutions of branched alkanes, alkenes, and alkynes, alkyl halides, ethers, alcohols, amides, amines, nitriles, alkyl nitrosos, alkyl nitrates, aldehydes, ketones, carboxylic acids, esters, and substituted aromatics.

260. A composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of
a bond distance between two of the atoms,
a bond angle between three of the atoms, and
a bond energy between two of the atoms,
orbital intercept distances and angles,

charge-density functions of atomic, hybridized, and molecular orbitals,
the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

261. A composition of matter according to claim 260, wherein the novel property is a new pharmaceutical use.

262. A composition of matter according to claim 261 that is novel, wherein the novel property is stability at room temperature of a new arrangement of atoms or ions.

263. A novel composition of matter discovered by calculating at least one of
a bond distance between two of the atoms,
a bond angle between three of the atoms, and
a bond energy between two of the atoms,
orbital intercept distances and angles,
charge-density functions of atomic, hybridized, and molecular orbitals,
the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

264. A system of determining at least one of
a bond distance between two of the atoms,
a bond angle between three of the atoms, and
a bond energy between two of the atoms,
orbital intercept distances and angles,
charge-density functions of atomic, hybridized, and molecular orbitals,
wherein the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that the bound electron(s) does not radiate under acceleration.

265. The system of claim 264, further comprising discovering a new composition of matter.

266. The system of claim 1, wherein the nature of said specie includes the nature of a chemical bond thereof.

267. The system of claim 1, wherein at least one bond angle between three atoms is computed and displayed.

268. The system of claim 1, wherein at least one bond distance between two atoms is computed and displayed.

269. The system of claim 1, wherein at least one geometric component is computed and displayed.

270. The system of claim 1, wherein at least one potential energy between an electron and a nucleus is computed.

271. The system of claim 1, wherein at least one potential energy between two nuclei is computed.

272. The system of claim 1, wherein at least one kinetic energy of an electron is computed.

273. The system of claim 1, wherein at least one magnetic energy between electrons is computed.

274. The system of claim 1, wherein at least one total energy of a bond is computed.

275. The system of claim 1, wherein at least one change in atomic energy between atoms due to bonding is computed.

276. The system of claim 1, further comprising at least one database of functional groups and at least one database of molecules, molecular ions, and/or molecular radicals, characterized in that the functional groups, molecules, molecular ions, and molecular radicals having the nature of their chemical bonds computed by the Maxwillian solutions of charge, mass, and current density, or both databases being combined into one database or split into multiple databases, and the processing means being in communication with the databases or combined database.

277. The system of claim 1, further comprising at least one database of functional groups having the nature of their chemical bonds computed by the Maxwillian solutions of charge, mass, and current density.

278. The system of claim 276, further comprising means for selecting a desired first functional group, characterized in that the selected functional group is displayed with open bonds being displayed, means for selecting an open bond, means for selecting a second functional group to be bound to the first functional group, characterized in that the second functional group is displayed with open bonds being displayed, means for selecting an open bond on the second functional group, and means for combining the selected bonds, whereby at least a portion of a desired molecule is displayed.

279. The system of claim 276, further comprising selecting and combining functional groups until a desired molecule is displayed.

280. The system of claim 277, further comprising means for selecting a desired first functional group, characterized in that the selected functional group is displayed with open bonds being displayed, means for selecting an open bond, means for selecting a second functional group to be bound to the first functional group, characterized in that the second functional group is displayed with open bonds being displayed, means for selecting an open bond on the second functional group, and means for combining the selected bonds, whereby at least a portion of a desired molecule is displayed.

281. The system of claim 277, further comprising selecting and combining functional groups until a desired molecule is displayed.

282. The system of claim 1, further comprising a means for inputting the chemical structure of a desired molecule and parsing the inputted molecule into functional groups.

283. The system of claim 282, further comprising a database of functional groups having the nature of their chemical bonds computed by the Maxwillian solutions of charge, mass, and current density, characterized in that the processing means combines the functional groups and the desired molecule is displayed.

284. The system of claim 282, wherein the chemical structure is imputed using a Simplified Molecular Input Line Entry System.

285. The system of claim 283, wherein the chemical structure is imputed using a Simplified Molecular Input Line Entry System.

286. The system of claim 282, wherein the Simplified Molecular Input Line Entry System is SMILES.

287. The system of claim 283, wherein the Simplified Molecular Input Line Entry System is SMILES.

288. The system according to claim 1, wherein the force generalized constant k' of a H_2-type ellipsoidal MO due to the equivalent of two point charges at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \qquad (15.1)$$

where C_1 is the fraction of the H_2-type ellipsoidal molecular orbital basis function of a chemical bond of the specie and C_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond.

289. The system according to claim 1, wherein the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.2}$$

the internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.3}$$

the length of the semiminor axis of the prolate spheroidal MO $b = c$ is given by

$$b = \sqrt{a^2 - c'^2} \tag{15.4}$$

and, the eccentricity, e, is

$$e = \frac{c'}{a} \tag{15.5}.$$

290. The system according to claim 289, wherein a potential energy of the electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\varepsilon_o\sqrt{a^2 - b^2}} \ln\frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \tag{15.6}$$

where n_1 is the number of equivalent bonds of the MO for functional groups and in the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by c_{BO}, the bond-order factor, which is 1 for a single bond, 4 for an independent double bond and 9 for an independent triplet bond.

291. The system according to claim 1, wherein the potential energy of the two nuclei is

$$V_p = n_1 \frac{e^2}{8\pi\varepsilon_o\sqrt{a^2 - b^2}} \tag{15.7}.$$

292. The system according to claim 1, wherein the kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{15.8}$$

where n_1 is the number of equivalent bonds of the MO for functional groups and in the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by c_{BO}, the bond-order factor, which is 1 for a single bond, 4 for an independent double bond and 9 for an independent triplet bond.

293. The system according to claim 1, wherein the energy, V_m, of the magnetic force between the electrons is

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a\sqrt{a^2-b^2}} \ln \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} \tag{15.9}$$

where n_1 is the number of equivalent bonds of the MO for functional groups and in the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by c_{BO}, the bond-order factor, which is 1 for a single bond, 4 for an independent double bond and 9 for an independent triplet bond.

294. The system according to claim 1, wherein total energy of the H_2-type prolate spheroidal MO, $E_T(H_2MO)$, is given by the sum of the energy terms:

$$E_T(H_2MO) = V_e + T + V_m + V_p \tag{15.10}$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right] \\ &= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1 c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] \end{aligned} \tag{15.11}$$

where n_1 is the number of equivalent bonds of the MO for functional groups and in the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by c_{BO}, the bond-order factor, which is 1 for a single bond, 4 for an independent double bond and 9 for an independent triplet bond.

295. The system according to claim 1, wherein the total energy $E_T\left(atom, msp^3\right)$ (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one AO shell according to the formula:

$$E_T\left(atom, msp^3\right) = -\sum_{m=1}^{n} IP_m \qquad (15.12$$

where IP_m is the m th ionization energy (positive) of the atom.

296. The system according to claim 295, wherein the radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T\left(atom, msp^3\right)} \qquad (15.13).$$

297. The system according to claim 295, wherein the Coulombic energy $E_{Coulomb}\left(atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by

$$E_{Coulomb}\left(atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} \qquad (15.14).$$

298. The system of claim 296, wherein in the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r of the AO electron:

$$E(magnetic) = \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} = \frac{8\pi\mu_o\mu_B^2}{r^3} \qquad (15.15)$$

then, the energy $E\left(atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(atom, msp^3\right)$ and $E(magnetic)$:

$$E\left(atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2 r^3} \qquad (15.16).$$

299. The system according to claim 295, wherein the total energy $E_T\left(mol.atom, msp^3\right)$ (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$E_T\left(mol.atom, msp^3\right) = E\left(atom, msp^3\right) - \sum_{m=2}^{n} IP_m \tag{15.17}$$

where IP_m is the m th ionization energy (positive) of the atom and the sum of $-IP_1$ plus the hybridization energy is $E\left(atom, msp^3\right)$.

300. The system of claim 299, wherein the radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3} = \left(\sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25) \right) \frac{-e^2}{8\pi\varepsilon_0 E_T\left(mol.atom, msp^3\right)} \tag{15.18}$$

where $s = 1, 2, 3$ for a single, double, and triple bond, respectively.

301. The system of claim 299, wherein the Coulombic energy $E_{Coulomb}\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by

$$E_{Coulomb}\left(mol.atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} \tag{15.19}.$$

302. The system of claim 298, wherein in the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ at the initial radius r of the AO electron given by Eq. (15.15). Then, the energy $E\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom, msp^3\right)$ and $E(magnetic)$:

$$E\left(mol.atom, msp^3\right) = \frac{-e^2}{8\pi\varepsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} \tag{15.20}$$

$E_T\left(atom-atom,msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between $E\left(mol.atom,msp^3\right)$ and $E\left(atom,msp^3\right)$:

$$E_T\left(atom-atom,msp^3\right)=E\left(mol.atom,msp^3\right)-E\left(atom,msp^3\right) \quad (15.21).$$

303. The system of claim 295, wherein $E_{Coulomb}\left(mol.atom,msp^3\right)$ is one of:

$E_{Coulomb}\left(C_{ethylene},2sp^3\right)$, $E_{Coulomb}\left(C_{ethane},2sp^3\right)$, $E_{Coulomb}\left(C_{acetylene},2sp^3\right)$, and $E_{Coulomb}\left(C_{alkane},2sp^3\right)$;

$E_{Coulomb}\left(atom,msp^3\right)$ is one of $E_{Coulomb}\left(C,2sp^3\right)$ and $E_{Coulomb}\left(Cl,3sp^3\right)$;

$E\left(mol.atom,msp^3\right)$ is one of $E\left(C_{ethylene},2sp^3\right)$, $E\left(C_{ethane},2sp^3\right)$, $E\left(C_{acetylene},2sp^3\right)$ $E\left(C_{alkane},2sp^3\right)$;

$E\left(atom,msp^3\right)$ is one of and $E\left(C,2sp^3\right)$ and $E\left(Cl,3sp^3\right)$;

$E_T\left(atom-atom,msp^3\right)$ is one of $E\left(C-C,2sp^3\right)$, $E\left(C=C,2sp^3\right)$, and. $E\left(C\equiv C,2sp^3\right)$;

atom msp^3 is one of $C2sp^3$, $Cl3sp^3$

$E_T\left(atom-atom\left(s_1\right),msp^3\right)$ is $E_T\left(C-C,2sp^3\right)$ and $E_T\left(atom-atom\left(s_2\right),msp^3\right)$ is $E_T\left(C=C,2sp^3\right)$, and

r_{msp^3} is one of r_{C2sp^3}, $r_{ethane2sp^3}$, $r_{ethylene2sp^3}$, $r_{acetylene2sp^3}$, $r_{alkane2sp^3}$, and r_{Cl3sp^3}.

In the case of the $C2sp^3$ HO, the initial parameters (Eqs. (14.142-14.146)) are

$$r_{2sp^3}=\sum_{n=2}^{5}\frac{(Z-n)e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)}=\frac{10e^2}{8\pi\varepsilon_0\left(e148.25751\ eV\right)}=0.91771a_0 \quad (15.22)$$

$$E_{Coulomb}\left(C,2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}=\frac{-e^2}{8\pi\varepsilon_0 0.91771a_0}=-14.82575\ eV \quad (15.23)$$

$$E(magnetic)=\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}=\frac{8\pi\mu_o\mu_B^2}{\left(0.84317a_0\right)^3}=0.19086\ eV \quad (15.24)$$

$$E\left(C,2sp^3\right)=\frac{-e^2}{8\pi\varepsilon_0 r_{2sp^3}}+\frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(r_3\right)^3}$$
$$=-14.82575\ eV+0.19086\ eV \quad (15.25)$$
$$=-14.63489\ eV$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

304. The system of claim 300, wherein

$$\sum_{q=Z-n}^{Z-1}(Z-q)=10 \quad (15.26)$$

Equations (14.147) and (15.17) give

$$E_T\left(mol.atom,msp^3\right)=E_T\left(C_{ethane},2sp^3\right)=-151.61569\ eV \quad (15.27)$$

and using Eqs. (15.18-15.28), the final values of r_{C2sp^3}, $E_{Coulomb}\left(C2sp^3\right)$, and $E\left(C2sp^3\right)$, and the resulting $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ of the MO due to charge donation from the HO to the MO

where $C\overset{BO}{-}C$ refers to the bond order of the carbon-carbon bond for different values of the parameter s are given in Table 15.1.

Table 15.1:

MO Bond Order (BO)	s 1	s 2	$r_{C2sp^3}(a_0)$ Final	$E_{Coulomb}\left(C2sp^3\right)$(eV) Final	$E\left(C2sp^3\right)$ (eV) Final	$E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ (eV)
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
II	2	0	0.85252	-15.95955	-15.76868	-1.13379
III	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

305. The system of claim 295, wherein a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy $E\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell of each bonding atom is the average of $E\left(mol.atom, msp^3\right)$ for two different values of s:

$$E\left(mol.atom, msp^3\right) = \frac{E\left(mol.atom\left(s_1\right), msp^3\right) + E\left(mol.atom\left(s_2\right), msp^3\right)}{2} \qquad (15.28).$$

306. The system of claim 305, wherein in the case, $E_T\left(atom - atom, msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO, is average for two different values of s:

$$E_T\left(atom - atom, msp^3\right) = \frac{E_T\left(atom - atom\left(s_1\right), msp^3\right) + E_T\left(atom - atom\left(s_2\right), msp^3\right)}{2} \qquad (15.29).$$

307. The system of claim 305, wherein a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO comprises another AO or HO having a single bond order or a mixed bond order, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO, and in general, $E_T\left(atom - atom, msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO, is a weighted linear sum for different values of s that matches the energy of the bonded MOs, HOs, and AOs:

$$E_T\left(atom - atom, msp^3\right) = \sum_{n=1}^{N} c_{s_n} E_T\left(atom - atom\left(s_n\right), msp^3\right) \qquad (15.30)$$

where c_{s_n} is the multiple of the BO of s_n. The radius r_{msp^3} of the *atom* msp^3 shell of each bonding atom is given by the Coulombic energy using the initial energy $E_{Coulomb}\left(atom, msp^3\right)$ and $E_T\left(atom - atom, msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of each atom-atom-bond MO:

$$r_{msp^3} = \frac{-e^2}{8\pi\varepsilon_0 a_0 \left(E_{Coulomb}\left(atom, msp^3\right) + E_T\left(atom - atom, msp^3\right)\right)} \tag{15.31}$$

where $E_{Coulomb}\left(C2sp^3\right) = -14.825751\ eV$.

308. The system of claim 307, wherein the Coulombic energy $E_{Coulomb}\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by Eq. (15.19).

309. The system of claim 308, wherein in the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E\left(mol.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom, msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

310. The system of claim 308, wherein, $E_T\left(atom - atom, msp^3\right)$, the energy change of each *atom* msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between $E\left(mol.atom, msp^3\right)$ and $E\left(atom, msp^3\right)$ given by Eq. (15.21).

311. The system of claim 310, wherein using the equation (15.23) for $E_{Coulomb}\left(C, 2sp^3\right)$ in equation (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

312. The system of claim 295, wherein the radius r_{mol2sp^3} of the $C2sp^3$ HO of a carbon atom of a given specie is calculated using Eq. (14.514) by considering

$\sum E_{T_{mol}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which it participates in bonding.

313. The system of claim 1, wherein equation for the radius is given by

$$r_{mol2sp^3}=\frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{mol}}\left(MO,2sp^3\right)\right)}=\frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+\sum\left|E_{T_{mol}}\left(MO,2sp^3\right)\right|\right)} \quad (15.32).$$

314. The system of 295, wherein the Coulombic energy $E_{Coulomb}\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by Eq. (15.19).

315. The system of claim 295, in the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E\left(mol.atom,msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(mol.atom,msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

316. The system of claim 315, wherein for the $C2sp^3$ HO of each methyl group of an alkane contributes $-0.92918\ eV$ (Eq. (14.513)) to the corresponding single $C-C$ bond; the corresponding $C2sp^3$ HO radius is given by Eq. (14.514). The $C2sp^3$ HO of each methylene group of C_nH_{2n+2} contributes $-0.92918\ eV$ to each of the two corresponding $C-C$ bond MOs, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

317. The system of claim 316, wherein the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

$$r_{alkaneC_{methylene}2sp^3} = \frac{-e^2}{8\pi\varepsilon_0\left(E_{Coulomb}\left(C,2sp^3\right)+\sum E_{T_{alkane}}\left(methylene\ C-C,2sp^3\right)\right)}$$
$$= \frac{e^2}{8\pi\varepsilon_0\left(e14.825751\ eV+e0.92918\ eV+e0.92918\ eV\right)}$$
$$= 0.81549a_0$$

(15.33)

$$E_{Coulomb}\left(C_{methylene}2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0\left(0.81549a_0\right)} = -16.68412\ eV \quad (15.34)$$

$$E\left(C_{methylene}2sp^3\right) = \frac{-e^2}{8\pi\varepsilon_0\left(0.81549a_0\right)} + \frac{2\pi\mu_0 e^2\hbar^2}{m_e^2\left(0.84317a_0\right)^3} = -16.49325\ eV \quad (15.35)$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

318. The system of claim 316, wherein in the determination of the parameters of functional groups, heteroatoms bonding to $C2sp^3$ HOs to form MOs are energy matched to the $C2sp^3$ HOs, the radius and the energy parameters of a bonding heteroatom are given by the same equations as those for $C2sp^3$ HOs.

319. The system of claim 318, wherein using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO, $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom,msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ are calculated using $\sum E_{T_{group}}\left(MO,2sp^3\right)$, the total energy donation to each bond with which an atom participates in bonding corresponding to the values of $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2 and the final values of $r_{Atom.HO.AO}$, $E_{Coulomb}\left(mol.atom,msp^3\right)$, and $E\left(C_{mol}2sp^3\right)$ calculated using the values of $E_T\left(C\overset{BO}{-}C,C2sp^3\right)$ given in Tables 15.1 and 15.2 are shown in Tables 15.3A and 15.3B in the specification, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

320. The system of claim 319, wherein the energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO.

321. The system of claim 320, wherein the force constant k' (Eq. (15.1)) is used to determine the ellipsoidal parameter c' (Eq. (15.2)) of the each H_2-type-ellipsoidal-MO in terms of the central force of the foci, c' is substituted into the energy equation (from Eq. (15.11))) which is set equal to n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2, $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

322. The system of claim 321, wherein the energy equation and the relationship between the axes, the dimensions of the MO are solved, the energy equation has the semimajor axis a as it only parameter, the solution of the semimajor axis a allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)), and the parameter solutions then allow for the component and total energies of the MO to be determined.

323. The system of claim 1, wherein the total energy, $E_T(H_2MO)$, is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus $E_T(AO/HO)$:

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO) \quad (15.36)$$

$$E_T(H_2MO) = -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E_T(AO/HO)$$

$$=-\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T(AO/HO) \quad (15.37)$$

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2-type

ellipsoidal MO basis function of a chemical bond of the group, c_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and $E_T(AO/HO)$ is the total energy comprising the difference of the energy $E(AO/HO)$ of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component $\Delta E_{H_2MO}(AO/HO)$ due to the AO or HO's charge donation to the MO.

324. The system of claim 323, wherein

$$E_T(AO/HO) = E(AO/HO) - \Delta E_{H_2MO}(AO/HO) \quad (15.38)$$

325. The system of claim 324, wherein as specific examples, $E_T(AO/HO)$ is one from the group of

$E_T(AO/HO) = E(O2p\ shell) = -E(ionization;\ O) = -13.6181\ eV$;

$E_T(AO/HO) = E(N2p\ shell) = -E(ionization;\ N) = -14.53414\ eV$;

$E_T(AO/HO) = E(C, 2sp^3) = -14.63489\ eV$;

$E_T(AO/HO) = E_{Coulomb}(Cl, 3sp^3) = -14.60295\ eV$;

$E_T(AO/HO) = E(ionization;\ C) + E(ionization;\ C^+)$;

$E_T(AO/HO) = E(C_{ethane}, 2sp^3) = -15.35946\ eV$;

$E_T(AO/HO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3)$;

$E_T(AO/HO) = E(C, 2sp^3) - 2E_T(C=C, 2sp^3) = -14.63489\ eV - (-2.26758\ eV)$;

$E_T(AO/HO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002\ eV$;

$E_T(AO/HO) = E(C, 2sp^3) - 2E_T(C \equiv C, 2sp^3) = -14.63489\ eV - (-3.13026\ eV)$;

$E_T(AO/HO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3)$;

$E_T(AO/HO) = E(C, 2sp^3) - E_T(C=C, 2sp^3) = -14.63489\ eV - (-1.13379\ eV)$, and

$E_T(AO/HO) = E(C_{alkane}, 2sp^3) = -15.56407\ eV$, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

326. The system of claim 1, wherein to solve the bond parameters and energies, $c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}}$ (Eq. (15.2)) is substituted into $E_T(H_2MO)$ to give

$$E_T(H_2MO) = -\frac{n_1 e^2}{8\pi\varepsilon_o\sqrt{a^2-b^2}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}-1\right]+E_T(AO/HO)$$

$$= -\frac{n_1 e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T(AO/HO)$$

$$= -\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T(AO/HO)$$

(15.39)

wherein the total energy is set equal to $E(basis\ energies)$ which in the most general case is given by the sum of a first integer n_1 times the total energy of H_2 minus a second integer n_2 times the total energy of H, minus a third integer n_3 times the valence energy of $E(AO)$ (e.g. $E(N) = -14.53414\ eV$) where the first integer can be $1,2,3...$, and each of the second and third integers can be $0,1,2,3....$

327. The system of claim 326, wherein

$$E(basis\ energies) = n_1(-31.63536831\ eV) - n_2(-13.605804\ eV) - n_3E(AO)$$

(15.40)

in the case that the MO bonds two atoms other than hydrogen, $E(basis\ energies)$ is n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2, $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

$$E(basis\ energies) = n_1(-31.63536831\ eV) \quad (15.41)$$

$E_T(H_2MO)$, is set equal to $E(basis\ energies)$, and the semimajor axis a is solved.

328. The system of claims 289 or 326, wherein the semimajor axis a is solved from the equation of the form:

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$$-\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right]+E_T(AO/HO)=E(basis\ energies) \quad (15.42)$$

The distance from the origin of the H_2-type-ellipsoidal-MO to each focus c', the internuclear distance $2c'$, and the length of the semiminor axis of the prolate spheroidal H_2-type MO $b=c$ are solved from the semimajor axis a using Eqs. (15.2-15.4).

329. The system of claim 328, wherein the component energies are given by Eqs. (15.6-15.9) and (15.39).

330. The system of claim 323, wherein the total energy of the MO of the functional group, $E_T(MO)$, is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and $E_T\left(atom-atom, msp^3.AO\right)$, the change in the energy of the AOs or HOs upon forming the bond.

331. The system of claim 330, wherein from Eqs. (15.39-15.40), $E_T(MO)$ is

$$E_T(MO)=E(basis\ energies)+E_T\left(atom-atom, msp^3.AO\right) \quad (15.43)$$

332. The system of claim 331, wherein during bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy $\overline{E}_{osc}$ is the sum of the Doppler, $\overline{E}_D$, and average vibrational kinetic energies, $\overline{E}_{Kvib}$:

$$\overline{E}_{osc}=n_1\left(\overline{E}_D+\overline{E}_{Kvib}\right)=n_1\left(E_{h\nu}\sqrt{\frac{2\overline{E}_K}{m_ec^2}}+\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \quad (15.44)$$

where n_1 is the number of equivalent bonds of the MO, k is the spring constant of the equivalent harmonic oscillator, and μ is the reduced mass.

333. The system of claim 332, wherein the angular frequency of the reentrant oscillation in the transition state corresponding to $\overline{E}_D$ is determined by the force between the central

field and the electrons in the transition state.

334. The system of claim 333,wherein the force and its derivative are given by

$$f(R) = -c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \qquad (15.45)$$

and

$$f'(a) = 2c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \qquad (15.46)$$

such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}} \qquad (15.47)$$

where R is the semimajor axis a or the semiminor axis b depending on the eccentricity of the bond that is most representative of the oscillation in the transition state, c_{BO} is the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups, c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules and 9 for an independent triplet bond, C_{1o} is the fraction of the H_2-type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. Typically, $C_{1o} = C_1$ and $C_{2o} = C_2$, the kinetic energy, E_K, corresponding to $\overline{E}_D$ is given by Planck's equation for functional groups:

$$\overline{E}_K = \hbar\omega = \hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}} \qquad (15.48)$$

335. The system of claim 334, wherein the Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_D \cong E_{h\nu}\sqrt{\frac{2\overline{E}_K}{m_e c^2}} = E_{h\nu}\sqrt{\frac{2\hbar\sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}}}{m_e c^2}} \qquad (15.49)$$

$\overline{E}_{osc}$ given by the sum of $\overline{E}_D$ and $\overline{E}_{Kvib}$ is

$$\overline{E}_{osc}(group) = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_{hv}\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{m_e}}{m_e c^2}} + E_{vib}\right) \quad (15.50)$$

E_{hv} of a group having n_1 bonds is given by $E_T(MO)/n_1$ such that

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(E_T(MO)/n_1\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \quad (15.51)$$

$E_{T+osc}(Group)$ is given by the sum of $E_T(MO)$ (Eq. (15.42)) and $\overline{E}_{osc}$ (Eq. (15.51)):

$$E_{T+osc}(Group) = E_T(MO) + \overline{E}_{osc}$$

$$= \left(\left(\begin{array}{l} -\frac{n_1 e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}}-1\right] \\ +E_T\left(AO/HO\right)+E_T\left(atom-atom, msp^3.AO\right)\end{array}\right)\right.$$

$$\left.\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}{m_e c^2}}\right]+n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right)$$

$$= \left(E(basis\ energies)+E_T\left(atom-atom, msp^3.AO\right)\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{m_e}}{m_e c^2}}\right]+n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

(15.52).

336. The system of claim 335, wherein the total energy of the functional group $E_T(group)$ is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, $E(basis\ energies)$, the change in the energy of the AOs or HOs upon forming the bond ($E_T\left(atom-atom, msp^3.AO\right)$), the energy of

oscillation in the transition state, and the change in magnetic energy with bond formation, E_{mag}.

337. The system of claim 336, wherein from Eq. (15.52), the total energy of the group $E_T(Group)$ is

$$E_T(Group) = \left(\begin{array}{l} \left(E(basis\ energies) + E_T\left(atom - atom, msp^3.AO\right) \right) \left[1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}} \right] \\ + n_1 \overline{E}_{Kvib} + E_{mag} \end{array} \right) \quad (15.53).$$

338. The system of claim 337, wherein the change in magnetic energy E_{mag} which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

$$E_{mag} = c_3 \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \qquad (15.54)$$

where r^3 is the radius of the atom that reacts to form the bond and c_3 is the number of electron pairs.

$$E_T(Group) = \left(\begin{array}{l} \left(E(basis\ energies) + E_T\left(atom - atom, msp^3.AO\right) \right) \left[1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}} \right] \\ + n_1 \overline{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \end{array} \right) \quad (15.55).$$

339. The system of claim 338, wherein the total bond energy of the group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.55)) and the total energy of the starting species given by the sum of $c_4 E_{initial}(c_4\ AO/HO)$ and $c_5 E_{initial}(c_5\ AO/HO)$:

$$E_{D\,(Group)} = -\left(\begin{array}{l} \left(E(basis\ energies) + E_T\left(atom - atom, msp^3.AO\right)\right)\left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}}\right] \\ +n_1\overline{E}_{Kvib} + c_3\frac{8\pi\mu_o\mu_B^2}{r_n^3} - \left(c_4 E_{initial}\left(AO/HO\right) + c_5 E_{initial}\left(c_5\ AO/HO\right)\right) \end{array} \right)$$

(15.56).

340. The system of claim 336, wherein in the case of organic molecules, the atoms of the functional groups are energy matched to the $C2sp^3$ HO such that

$$E\left(AO/HO\right) = -14.63489\ eV \qquad (15.57)$$

For examples of E_{mag} from previous sections:

$$E_{mag}\left(C2sp^3\right) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{\left(0.91771a_0\right)^3} = c_3 0.14803\ eV \qquad (15.58)$$

$$E_{mag}\left(O2p\right) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{a_0^3} = c_3 0.11441\ eV \qquad (15.59)$$

$$E_{mag}\left(N2p\right) = c_3\frac{8\pi\mu_o\mu_B^2}{r^3} = c_3\frac{8\pi\mu_o\mu_B^2}{\left(0.93084a_0\right)^3} = c_3 0.14185\ eV \quad (15.60).$$

341. The system of claim 340, wherein in the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at a, the remaining parameters are determined using Eqs. (15.1-15.5), the energies are given by Eqs. (15.52-15.59), and to meet the equipotential condition for the union of the H_2-type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor c_2 of a H_2-type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

(i) one:

$$c_2 = 1 \quad (15.61)$$

(ii) the ratio that is less than one of $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the

Coulombic energy of the participating AO or HO of the atom, $E_{Coulomb}\left(MO.atom, msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|$>13.605804 eV :

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|} \quad (15.62)$$

For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|$<13.605804 eV :

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|}{13.605804\ eV} \quad (15.63)$$

(iii) the ratio that is less than one of 13.605804 eV , the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the valence energy, $E(valence)$, of the participating AO or HO of the atom where $E(valence)$ is the ionization energy or $E\left(MO.atom, msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32). For $|E(valence)|$>13.605804 eV :

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}} = \frac{13.605804\ eV}{|E(valence)|} \quad (15.64)$$

For $|E(valence)|$<13.605804 eV :

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B\ AorBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{|E(valence)|}{13.605804\ eV} \quad (15.65)$$

(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom, $E_{Coulomb}\left(MO.atom, msp^3\right)$ given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, $E(valence)$, of the participating AO or HO of a second atom to which the first is energy matched where $E(valence)$ is the

ionization energy or $E\left(MO.atom,msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right| > E(valence)$:

$$c_2 = \frac{|E(valence)|}{\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|} \qquad (15.66)$$

For $\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right| < E(valence)$:

$$c_2 = \frac{\left|E_{Coulomb}\left(MO.atom,msp^3\right)\right|}{|E(valence)|} \qquad (15.67)$$

(v) the ratio that is less than one of the magnitude of the valence-level energies, $E_n(valence)$, of the AO or HO of the nth participating atom of two that are energy matched where $E(valence)$ is the ionization energy or $E\left(MO.atom,msp^3\right)$ given by Eqs. (15.20) and (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)} \qquad (15.68)$$

(vi) the factor that is the ratio of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.68); alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \qquad (15.69)$$

(vii) the factor that is the product of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.69); alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of

atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) \qquad (15.70)$$

The hybridization factor c_2 corresponds to the force constant k (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), then C_2 corresponding to k' (Eq. (15.1)) is given by Eqs. (15.62-15.70).

342. The system of claim 341, wherein specific examples of the factors c_2 and C_2 of a H_2-type ellipsoidal MO of Eq. (15.51) given in following sections are

$$c_2(C2sp^3HO\ to\ F) = \frac{E(C,2sp^3)}{E(F)} c_2(C2sp^3HO) = \frac{-14.63489\ eV}{-17.42282\ eV}(0.91771) = 0.77087;$$

$$C_2(C2sp^3HO\ to\ Cl) = \frac{E(Cl)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-12.96764\ eV}{-14.63489\ eV}(0.91771) = 0.81317;$$

$$C_2(C2sp^3HO\ to\ Br) = \frac{E(Br)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-11.81381\ eV}{-14.63489\ eV}(0.91771) = 0.74081;$$

$$C_2(C2sp^3HO\ to\ I) = \frac{E(I)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-10.45126\ eV}{-14.63489\ eV}(0.91771) = 0.65537;$$

$$c_2(C2sp^3HO\ to\ O) = \frac{E(O)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-13.61806\ eV}{-14.63489\ eV}(0.91771) = 0.85395;$$

$$c_2(H\ to\ 1°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.35946\ eV} = 0.94627;$$

$$c_2(C2sp^3HO\ to\ N) = \frac{E(N)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-14.53414\ eV}{-14.63489\ eV}(0.91771) = 0.91140;$$

$$c_2(H\ to\ 2°N) = \frac{E(N)}{E(C,2sp^3)} = \frac{-14.53414\ eV}{-15.56407\ eV} = 0.93383;$$

$$C_2(S3p\ to\ H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001\ eV}{-13.60580\ eV} = 0.76144;$$

$$C_2(C2sp^3HO\ to\ \mathrm{S}) = \frac{E(S)}{E(C,2sp^3)} c_2(C2sp^3HO) = \frac{-10.36001\ eV}{-14.63489\ eV}(0.91771) = 0.64965;$$

$$c_2\left(O\ to\ S3sp^3\ to\ C2sp^3HO\right)=\frac{E(O)}{E(S)}c_2\left(C2sp^3HO\right)$$
$$=\frac{-13.61806\ eV}{-10.36001\ eV}(0.91771);$$
$$=1.20632$$

$$c_2\left(S3sp^3\right)=\frac{E_{Coulomb}\left(S3sp^3\right)}{E(H)}=\frac{-11.57099\ eV}{-13.60580\ eV}=0.85045;$$

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right)=\frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right)=\frac{-11.52126\ eV}{-14.63489\ eV}(0.85045)=0.66951;$$

$$C_2\left(S3sp^3\ to\ O\ to\ C2sp^3HO\right)=\frac{E\left(S,3sp^3\right)}{E(O,2p)}c_2\left(C2sp^3HO\right)$$
$$=\frac{-11.52126\ eV}{-13.61806\ eV}(0.91771)\ ;$$
$$=0.77641$$

$$c_2\left(O\ to\ N2p\ to\ C2sp^3HO\right)=\frac{E(O)}{E(N)}c_2\left(C2sp^3HO\right)$$
$$=\frac{-13.61806\ eV}{-14.53414\ eV}(0.91771);$$
$$=0.85987$$

$$c_2\left(N2p\ to\ O2p\right)=\frac{c_2\left(C2sp^3HO\ to\ N\right)}{c_2\left(C2sp^3HO\ to\ O\right)}=\frac{0.91140}{0.85395}=1.06727;$$

$$C_2\left(benzeneC2sp^3HO\right)=c_2\left(benzeneC2sp^3HO\right)=\frac{13.605804\ eV}{15.95955\ eV}=0.85252;$$

$$c_2\left(arylC2sp^3HO\ to\ O\right)=\frac{E(O)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)$$
$$=\frac{-13.61806\ eV}{-14.63489\ eV}(0.85252)\qquad;$$
$$=0.79329$$

$$c_2\left(H\ to\ \text{anline}\ N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}=\frac{-14.53414\ eV}{-15.76868\ eV}=0.92171,$$

$$c_2\left(arylC2sp^3HO\ to\ N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)$$
$$=\frac{-14.53414\ eV}{-14.63489\ eV}(0.85252)$$
$$=0.84665$$

$$c_2\left(H \text{ to anline } N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}=\frac{-14.53414\ eV}{-15.76868\ eV}=0.92171;$$

$$c_2\left(arylC2sp^3HO \text{ to } N\right)=\frac{E(N)}{E\left(C,2sp^3\right)}c_2\left(arylC2sp^3HO\right)$$

$$=\frac{-14.53414\ eV}{-14.63489\ eV}(0.85252) \quad , \quad \text{and}$$

$$=0.84665$$

$$C_2\left(S3p \text{ to aryl-type } C2sp^3HO\right)=\frac{E\left(S,3p\right)}{E\left(C,2sp^3\right)}=\frac{-10.36001\ eV}{-15.76868\ eV}=0.65700.$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

343. The system of claim 1, wherein the parameters of the point of intersection of each H_2-type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r=r_0\frac{1+e}{1+e\cos\theta'} \qquad (15.71).$$

344. The system of claim 343, wherein the radius of the A shell is r_A, and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_A=(a-c')\frac{1+\frac{c'}{a}}{1+\frac{c'}{a}\cos\theta'} \qquad (15.72).$$

345. The system of claim 344, wherein the polar angle θ' at the intersection point is given by

$$\theta'=\cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{a_0}-1\right)\right) \qquad (15.73).$$

346. The system of claim 345, wherein the angle $\theta_{A\,AO}$ the radial vector of the A AO makes with the internuclear axis is

$$\theta_{A\,AO} = 180° - \theta' \qquad (15.74).$$

347. The system of claim 345, wherein the distance from the point of intersection of the orbitals to the internuclear axis is the same for both component orbitals such that the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of each H_2-type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A \sin\theta_{A\,AO} = b \sin\theta_{H_2MO} \qquad (15.75)$$

such that

$$\theta_{H_2MO} = \sin^{-1}\frac{r_a \sin\theta_{A\,AO}}{b} \qquad (15.76).$$

348. The system of claim 347, wherein the distance d_{H_2MO} along the internuclear axis from the origin of H_2-type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a\cos\theta_{H_2MO} \qquad (15.77).$$

349. The system of claim 347, wherein the distance $d_{A\,AO}$ along the internuclear axis from the origin of the A atom to the point of intersection of the orbitals is given by

$$d_{A\,AO} = c' - d_{H_2MO} \qquad (15.78).$$

350. The system of claim 1, wherein in ACB MO comprising a linear combination of $C-A$-bond and $C-B$-bond MOs where C is the general central atom and a bond is possible between the A and B atoms of the $C-A$ and $C-B$ bonds, the $\angle ACB$ bond angle is determined by the condition that the total energy of the H_2-type ellipsoidal MO between the terminal A and B atoms is zero.

351. The system of claim 350, wherein the force constant k' of a H_2-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_o} \qquad (15.79)$$

where C_1 is the fraction of the H_2-type ellipsoidal MO basis function of a chemical bond of the specie which is 0.75 (Eq. (13.59)) for a terminal $A-H$ (A is H or other atom) and 1

otherwise and C_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52).

352. The system of claim 351, wherein the distance from the origin of the MO to each focus c' of the $A-B$ ellipsoidal MO is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}} \qquad (15.80).$$

353. The system of claim 351, wherein the internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \qquad (15.81).$$

354. The system of claim 351, wherein the length of the semiminor axis of the prolate spheroidal $A-B$ MO $b=c$ is given by Eq. (15.4).

355. The system of claim 351, wherein the component energies and the total energy, $E_T(H_2MO)$, of the $A-B$ bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of H_2 except that the terms based on charge are multiplied by c_{BO}, the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules.

356. The system of claim 355, wherein the kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond, the electron energy terms are multiplied by c_1, the fraction of the H_2-type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal $A-H$ (A is H or other atom) and 1 otherwise.

357. The system of claim 355, wherein the electron energy terms are further multiplied by c_2', the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond.

358. The system of claim 350, wherein when $A-B$ comprises atoms other than H, $E_T\left(atom-atom, msp^3.AO\right)$, the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give $E_T(H_2MO)$:

$$E_T(H_2MO)=\frac{-e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T\left(atom-atom, msp^3.AO\right)$$

(15.82).

359. The system of claim 350, the radiation reaction force in the case of the vibration of $A-B$ in the transition state corresponds to the Doppler energy, E_D, given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei.

360. The system of claim 359, wherein the total energy that includes the radiation reaction of the $A-B$ MO is given by the sum of $E_T(H_2MO)$ (Eq. (15.82)) and $\overline{E}_{osc}$ given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240).

361. The system of claim 360, wherein the total energy $E_T\left(A-B\right)$ of the $A-B$ MO including the Doppler term is

$$E_T\left(A-B\right)=\left[\left(\frac{-e^2}{8\pi\varepsilon_0 c'}\left[c_1c_2'\left(2c_{BO}-c'_{BO}\frac{a_0}{a}\right)\ln\frac{a+c'}{a-c'}-1\right]+E_T\left(atom-atom, msp^3.AO\right)\right)\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_ec^2}}\right]+\frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_1c_2'e^2}{8\pi\varepsilon_o a^3}-\frac{c_{BO}e^2}{8\pi\varepsilon_o\left(a+c'\right)^3}}{\mu}}\right]$$

(15.83)

where C_{1o} is the fraction of the H_2-type ellipsoidal MO basis function of the oscillatory transition state of the $A-B$ bond which is 0.75 (Eq. (13.233)) in the case of H bonding to a central atom and 1 otherwise, C_{2o} is the factor that results in an equipotential energy match of

the participating at least two atomic orbitals of the transition state of the chemical bond, and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the nuclei given by Eq. (11.154).

362. The system of claim 361, wherein to match the boundary condition that the total energy of the $A-B$ ellipsoidal MO is zero, $E_T(A-B)$ given by Eq. (15.83) is set equal to zero and substitution of Eq. (15.81) into Eq. (15.83) gives

$$0 = \left[\left(\frac{-e^2}{8\pi\varepsilon_0 \sqrt{\frac{aa_0}{2C_1C_2}}} \left[c_1 c_2' \left(2c_{BO} - c'_{BO} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1C_2}}}{a - \sqrt{\frac{aa_0}{2C_1C_2}}} - 1 \right] + E_T\left(atom - atom, msp^3.AO\right) \right) \right.$$
$$\left. \left[1 + \sqrt{\frac{2\hbar \sqrt{\frac{c_{BO} \frac{C_{1o} C_{2o} e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}} \right] + \frac{1}{2}\hbar \sqrt{\frac{c_{BO} \frac{c_1 c_2' e^2}{8\pi\varepsilon_o a^3} - \frac{c_{BO} e^2}{8\pi\varepsilon_o \left(a + \sqrt{\frac{aa_0}{2C_1C_2}} \right)^3}}{\mu}} \right] \quad (15.84).$$

363. The system of claim 362, wherein the vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)).

364. The system of claim 362, wherein the electron-central-field force and its derivative are given by

$$f(a) = -c_{BO} \frac{c_1 c_2' e^2}{4\pi\varepsilon_0 a^3} \quad (15.85)$$

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2' e^2}{4\pi\varepsilon_0 a^3} \quad (15.86).$$

365. The system of claim 364, wherein the nuclear repulsion force and its derivative are given by

$$f(a+c') = \frac{e^2}{8\pi\varepsilon_o (a+c')^2} \quad (15.87)$$

and

$$f'(a+c') = -\frac{e^2}{4\pi\varepsilon_o (a+c')^3} \quad (15.88)$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a} f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO}\frac{c_1 c_2' e^2}{4\pi\varepsilon_0 a^3} - \frac{e^2}{8\pi\varepsilon_0 (a+c')^2}}{\mu}} \quad (15.89).$$

366. The system of claim 365, wherein since both terms of $\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$ are small due to the large values of a and c', an approximation of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \left[\left(\frac{-e^2}{8\pi\varepsilon_0\sqrt{\frac{aa_0}{2C_1C_2}}}\left[c_1c_2'\left(2-\frac{a_0}{a}\right)\ln\frac{a+\sqrt{\frac{aa_0}{2C_1C_2}}}{a-\sqrt{\frac{aa_0}{2C_1C_2}}} - 1\right] + E_T\left(atom-atom, msp^3.AO\right)\right)\right.$$
$$\left.\left[1+\sqrt{\frac{2\hbar\sqrt{\frac{\frac{c_1e^2}{4\pi\varepsilon_o a^3}}{m_e}}}{m_e c^2}}\right] + \frac{1}{2}\hbar\sqrt{\frac{\frac{c_1e^2}{8\pi\varepsilon_o a^3} - \frac{e^2}{8\pi\varepsilon_o\left(a+\sqrt{\frac{aa_0}{2C_1C_2}}\right)^3}}{\mu}}\right] \quad (15.90).$$

367. The system of claim 366, wherein from the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the $A-B$ MO can be solved.

368. The system of claim 367, wherein Eq. (15.90) is solved by the reiterative technique using a computer.

369. The system of claim 366, wherein a factor c_2 of a given atom in the determination of c_2' for calculating the zero of the total $A-B$ bond energy is given by Eqs. (15.62-15.65).

370. The system of claim 369, wherein in the case of a $H-H$ terminal bond of an alkyl or alkenyl group, c_2' is the ratio of c_2 of Eq. (15.62) for the $H-H$ bond which is one and c_2 of the carbon of the corresponding $C-H$ bond:

$$c_2' = \frac{1}{c_2(C2sp^3)} = \frac{13.605804\ eV}{E_{Coulomb}\left(C-H\ C2sp^3\right)} \qquad (15.91)$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

371. The system of claim 366, wherein in the case of the determination of the bond angle of the ACH MO comprising a linear combination of $C-A$ -bond and $C-H$ -bond MOs where A and C are general, C is the central atom, and c_2 for an atom is given by Eqs. (15.62-15.70), c_2' of the $A-H$ terminal bond is the ratio of c_2 of the A atom for the $A-H$ terminal bond and c_2 of the C atom of the corresponding $C-H$ bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3)} \qquad (15.92).$$

372. The system of claim 366, wherein in the case of the determination of the bond angle of the COH MO of an alcohol comprising a linear combination of $C-O$-bond and $O-H$ -bond MOs where C, O, and H are carbon, oxygen, and hydrogen, respectively, c_2' of the $C-H$ terminal bond is 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the $C2sp^3$ HO, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

373. The system of claim 366, wherein in the determination of the hybridization factor c_2' of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy, $E_{Coulomb}\left(MO.atom, msp^3\right)$, or the energy, $E\left(MO.atom, msp^3\right)$, the radius $r_{A-B\ AorBsp^3}$ of the A or B AO or HO of the heteroatom of the $A-B$ terminal bond MO such as the $C2sp^3$ HO of a terminal $C-C$

bond is calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}\left(MO, 2sp^3\right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond.

374. The system of claim 373, wherein the Coulombic energy $E_{Coulomb}\left(MO.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by Eq. (15.19).

375. The system of claim 374, wherein in the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy $E(magnetic)$ (Eq. (15.15)) at the initial radius r of the AO electron, and the energy $E\left(MO.atom, msp^3\right)$ of the outer electron of the *atom* msp^3 shell is given by the sum of $E_{Coulomb}\left(MO.atom, msp^3\right)$ and $E(magnetic)$ (Eq. (15.20)).

376. The system of claim 365, wherein in the specific case of the terminal bonding of two carbon atoms, the c_2 factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy $E_{Coulomb}\left(C-C\ C2sp^3\right)$ of the outer electron of the $C2sp^3$ shell given by Eq. (15.19) with the radius $r_{C-C\ C2sp^3}$ of each $C2sp^3$ HO of the terminal $C-C$ bond calculated using Eq. (15.32) by considering $\sum E_{T_{mol}}\left(MO, 2sp^3\right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, 0.92918 eV (Eq. (14.513)), corresponding to the terminal $C-C$ bond. The corresponding $E_T\left(atom-atom, msp^3.AO\right)$ in Eq. (15.90) is $E_T\left(C-C\ C2sp^3\right)=-1.85836\ eV$, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

377. The system of claim 366, wherein in the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus, c_2' is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

$$c_2' = \frac{1}{2}\left(c_2'\left(atom\ 1\right) + c_2'\left(atom\ 2\right)\right) \qquad (15.93)$$

In the exemplary cases of $C-C$, $O-O$, and $N-N$ where C is carbon:

$$c_2' = \frac{1}{2}\left(\frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-A\ A_1AO/HO}}} + \frac{\frac{e^2}{8\pi\varepsilon_0 a_0}}{\frac{e^2}{8\pi\varepsilon_0 r_{A-A\ A_2AO/HO}}}\right) \qquad (15.94)$$

$$= \frac{1}{2}\left(\frac{13.605804\ eV}{E_{Coulomb}\left(A-A.A_1AO/HO\right)} + \frac{13.605804\ eV}{E_{Coulomb}\left(A-A.A_2AO/HO\right)}\right)$$

In the exemplary cases of $C-N$, $C-O$, and $C-S$,

$$c_2' = \frac{1}{2}\left(\frac{13.605804\ eV}{E_{Coulomb}\left(C-B\ C2sp^3\right)} + c_2\left(C\ to\ B\right)\right) \qquad (15.95)$$

where C is carbon and $c_2\left(C\ to\ B\right)$ is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom B to that of the atom C in the group.

378. The system of claim 363, wherein the corresponding $E_T\left(atom-atom, msp^3.AO\right)$ term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

$E_T\left(C-O\ C2sp^3.O2p\right) = -1.44915\ eV$; $E_T\left(C-O\ C2sp^3.O2p\right) = -1.65376\ eV$;

$E_T\left(C-N\ C2sp^3.N2p\right) = -1.44915\ eV$; $E_T\left(C-S\ C2sp^3.S2p\right) = -0.72457\ eV$;

$E_T\left(O-O\ O2p.O2p\right) = -1.44915\ eV$; $E_T\left(O-O\ O2p.O2p\right) = -1.65376\ eV$;

$E_T\left(N-N\ N2p.N2p\right) = -1.44915\ eV$; $E_T\left(N-O\ N2p.O2p\right) = -1.44915\ eV$;

$E_T\left(F-F\ F2p.F2p\right) = -1.44915\ eV$; $E_T\left(Cl-Cl\ Cl3p.Cl3p\right) = -0.92918\ eV$;

$E_T\left(Br-Br\ Br4p.Br4p\right) = -0.92918\ eV$; $E_T\left(I-I\ I5p.I5p\right) = -0.36229\ eV$;

$E_T\left(C-F\ C2sp^3.F2p\right) = -1.85836\ eV$; $E_T\left(C-Cl\ C2sp^3.Cl3p\right) = -0.92918\ eV$;

$E_T\left(C-Br\ C2sp^3.Br4p\right) = -0.72457\ eV$; $E_T\left(C-I\ C2sp^3.I5p\right) = -0.36228\ eV$, and

$E_T\left(O-Cl\ O2p.Cl3p\right) = -0.92918\ eV$, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to + 10%, if desired.

379. The system of claim 366, wherein in the case that the terminal bond is $X-X$ where X is a halogen atom, c_1 is one, and c_2' is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where $E_{Coulomb}\left(MO.atom, msp^3\right)$ is determined using Eq. (15.32) and $E_{Coulomb}\left(MO.atom, msp^3\right)=13.605804\ eV$ for $X=I$.

380. The system of claim 379, wherein the factor C_1 of Eq. (15.90) is one for all halogen atoms.

381. The system of claim 379, wherein the factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

382. The system of claim 379, wherein for each of the halogens, Cl, Br, and I, C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2(1)$ being that of the halogen given by Eq. (15.68) that matches the valence energy of X ($E_1\left(valence\right)$) to that of the $C2sp^3$ HO ($E_2\left(valence\right)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2)=0.91771$, Eq. (13.430)), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

383. The system of claim 382, wherein $E_T\left(atom-atom, msp^3.AO\right)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.44915\ eV$, $-0.92918\ eV$, $-0.92918\ eV$, and $-0.33582\ eV$ for F, Cl, Br, and I, respectively, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

384. The system of claim 366, wherein in the case that the terminal bond is $C-X$ where C is a carbon atom and X is a halogen atom, the factors c_1 and C_1 of Eq. (15.90) are one for all halogen atoms.

385. The system of claim 384, wherein for $X=F$, c_2' is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and F atoms where c_2 for carbon is given by Eq. (15.62) and c_2 for fluorine matched to carbon is given by Eq. (15.70) with $c_2(1)$ for the fluorine atom given by Eq. (15.68) that matches the valence energy of F ($E_1(valence)=-17.42282\ eV$) to that of the $C2sp^3$ HO ($E_2(valence)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2)=0.91771$, Eq. (13.430)), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

386. The system of claim 385, wherein the factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

387. The system of claim 385, wherein for each of the other halogens, Cl, Br, and I, c_2' is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom.

388. The system of claim 387, wherein the C_2 of the terminal-atom bond matches that used to determine the energies of the corresponding $C-X$ -bond MO.

389. The system of claim 388, wherein C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2(1)$ for the halogen atom given by Eq. (15.68) that matches the valence energy of X ($E_1(valence)$) to that of the $C2sp^3$ HO ($E_2(valence)=-14.63489\ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO

($c_2(2) = 0.91771$, Eq. (13.430)), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

390. The system of claim 385, wherein $E_T\left(atom-atom, msp^3.AO\right)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.85836\ eV$, $-0.92918\ eV$, $-0.72457\ eV$, and $-0.33582\ eV$ for F, Cl, Br, and I, respectively, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

391. The system of claim 385, wherein in the case that the terminal bond is $H-X$ corresponding to the angle of the atoms HCX where C is a carbon atom and X is a halogen atom, the factors c_1 and C_1 of Eq. (15.90) are 0.75 for all halogen atoms.

392. The system of claim 385, wherein for $X = F$, c_2' is given by Eq. (15.69) with c_2 of the participating carbon and F atoms given by Eq. (15.62) and Eq. (15.65), respectively.

393. The system of claim 392, wherein the factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that $13.605804\ eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

394. The system of claim 393, wherein for each of the other halogens, Cl, Br, and I, c_2' is also given by Eq. (15.69) with c_2 of the participating carbon given by Eq. (15.62) and c_2 of the participating X atom given by $c_2 = 0.91771$ (Eq. (13.430)) since the X atom is energy matched to the $C2sp^3$ HO.

395. The system of claim 394, wherein C_2 is given by Eq. (15.65) for the corresponding atom X where C_2 matches the energy of the atom X to that of H.

396. The system of claim 366, wherein the distance between the two atoms A and B of the general molecular group ACB when the total energy of the corresponding $A-B$ MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1 s_2 \text{cosine}\theta = s_3^2 \quad (15.96).$$

397. The system of claim 396, wherein with $s_1 = 2c'_{C-A}$, the internuclear distance of the $C-A$ bond, $s_2 = 2c'_{C-B}$, the internuclear distance of each $C-B$ bond, and $s_3 = 2c'_{A-B}$, the internuclear distance of the two terminal atoms, the bond angle $\theta_{\angle ACB}$ between the $C-A$ and $C-B$ bonds is given by

$$(2c'_{C-A})^2 + (2c'_{C-B})^2 - 2(2c'_{C-A})(2c'_{C-B})\text{cosine}\theta = (2c'_{A-B})^2 \quad (15.97)$$

$$\theta_{\angle ACB} = \cos^{-1}\left(\frac{(2c'_{C-A})^2 + (2c'_{C-B})^2 - (2c'_{A-B})^2}{2(2c'_{C-A})(2c'_{C-B})}\right) \quad (15.98).$$

398. The system of claim 397, wherein the structure $C_b C_a(O_a)O_b$ wherein C_a is bound to C_b, O_a, and O_b, the three bonds are coplanar and two of the angles are known, say θ_1 and θ_2, then the third θ_3 can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \quad (15.99)$$

399. The system of claim 397, wherein in the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say θ_1, then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2} \quad (15.100).$$

400. The system of claim 1, wherein in the general case where the group comprises three $A-B$ bonds having B as the central atom at the apex of a pyramidal structure formed by the three bonds with the A atoms at the base in the xy-plane.

401. The system of claim 400, wherein the C_{3v} axis centered on B is defined as the vertical or z-axis, and any two $A-B$ bonds form an isosceles triangle, and the angle of

the bonds and the distances from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance $d_{origin-B}$ from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60°} \quad (15.101)$$

the height along the z-axis from the origin to the A nucleus d_{height} is given by

$$d_{height} = \sqrt{\left(2c'_{A-B}\right)^2 - \left(d_{origin-B}\right)^2}, \text{ and } (15.102)$$

the angle θ_v of each $A-B$ bond from the z-axis is given by

$$\theta_v = \tan^{-1}\left(\frac{d_{origin-B}}{d_{height}}\right) \quad (15.103).$$

402. The system of claim 401, wherein in the case where the central atom B is further bound to a fourth atom C and the $B-C$ bond is along the z-axis. Then, the bond $\theta_{\angle ABC}$ given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_v \quad (15.104).$$

403. The system of claim 400, wherein in the plane defined by a general ACA MO comprising a linear combination of two $C-A$-bond MOs where C is the central atom, the dihedral angle $\theta_{\angle BC/ACA}$ between the ACA-plane and a line defined by a third bond with C, specifically that corresponding to a $C-B$-bond MO, is calculated from the bond angle $\theta_{\angle ACA}$ and the distances between the A, B, and C atoms.

404. The system of claim 403, wherein the distance d_1 along the bisector of $\theta_{\angle ACA}$ from C to the internuclear-distance line between A and A, $2c'_{A-A}$, is given by

$$d_1 = 2c'_{C-A}\cos\frac{\theta_{\angle ACA}}{2} \quad (15.105)$$

where $2c'_{C-A}$ is the internuclear distance between A and C.

405. The system of claim 404, wherein the atoms A, A, and B define the base of a pyramid.

406. The system of claim 405, wherein the pyramidal angle $\theta_{\angle ABA}$ can be solved from the internuclear distances between A and A, $2c'_{A-A}$, and between A and B, $2c'_{A-B}$, using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1}\left(\frac{(2c'_{A-B})^2 + (2c'_{A-B})^2 - (2c'_{A-A})^2}{2(2c'_{A-B})(2c'_{A-B})}\right) \quad (15.106).$$

407. The system of claim 406, wherein the distance d_2 along the bisector of $\theta_{\angle ABA}$ from B to the internuclear-distance line $2c'_{A-A}$, is given by

$$d_2 = 2c'_{A-B}\cos\frac{\theta_{\angle ABA}}{2} \quad (15.107).$$

408. The system of claim 407, wherein the lengths d_1, d_2, and $2c'_{C-B}$ define a triangle wherein the angle between d_1 and the internuclear distance between B and C, $2c'_{C-B}$, is the dihedral angle $\theta_{\angle BC/ACA}$ that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1}\left(\frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{B-C})}\right) \quad (15.108).$$

409. The system of claim 1, wherein the specie are solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions, each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination, each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitsphere solutions bridged by molecular orbitals comprised of the H_2-type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section, the energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs, the energy E_{mag} (e.g. given by Eq. (15.58)) for a $C2sp^3$ HO and Eq.(15.59) for an $O2p$ AO) was subtracted for each set of unpaired electrons created by bond breakage.

410. They system of claim 409, wherein the bond energy is not equal to the component energy of each bond as it exists in the specie, although, they are close.

411. The system of claim 409, wherein the total energy of each group is its contribution to the total energy of the specie as a whole.

412. The system of claim 409, wherein the determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage.

413. The system of claim 409, wherein the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group, which will effect the functional-group energy, however because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they are neglected.

414. The system of claim 409, wherein the energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and $E\left(C,2sp^3\right)=-14.63489\ eV$ (Eq. (13.428)).

415. The system of claim 409, wherein the intercept angles are determined from Eqs. (15.71-15.78) using the final radius of the HO of each atom.

416. The system of claim 409, wherein a final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined.

417. The system of claim 416, wherein the final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius.

418. The system of claim 417, wherein the radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell.

419. The system of claim 416, wherein the donation of electron density to the AOs and HOs reduces the energy.

420. The system of claim 419, wherein the donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

421. The system of claim 1, wherein the molecular solutions are used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation.

422. The system of claim 1, wherein the new stable compositions of matter are predicted as well as the structures of combinatorial chemistry reactions.

423. The system of claim 1, wherein pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the specie to be identified from the common spatial charge-density functions of a series of active species.

424. The system of claim 1, wherein novel drugs are designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the drug.

425. The system of claim 1, wherein to calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given specie are used to calculate the fields, and from the fields, the interactions between groups of the same specie or between groups on different species are calculated wherein the interactions are distance and relative orientation dependent.

426. The system of claim 425, the fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

427. The system of claim 1, wherein in the case where three sets of $C=C$-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons, and each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2-type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\begin{pmatrix} 3\left(2\ C2sp^3 + 0.75\ H_2\ MO\right) \rightarrow 3\left(\overset{4e}{C=C}\right) - ethylene - type - bond\ MO \\ \rightarrow 6\left(\overset{3e}{C=C}\right) - bond\ MO\ of\ benzene \end{pmatrix} \quad (15.142).$$

428. The system of claim 427, wherein the linear combination of each H_2-type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the $C=C$-bond MO to achieve an energy minimum.

429. The system of claim 427, wherein the dimensional parameters of each bond $C=C$-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the $C=C$-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

430. The system of claim 427, wherein hybridization with 25% electron donation to each $C=C$-bond gives rise to the $C_{benzene}2sp^3$ HO-shell Coulombic energy $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$ given by Eq. (14.245).

431. The system of claim 427, wherein to meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and C_2 of Eq. (15.42) for the aromatic $\overset{3e}{C=C}$-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$ (Eq.

(14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2\left(benzeneC2sp^3HO\right)= c_2\left(benzeneC2sp^3HO\right)= \frac{13.605804\ eV}{15.95955\ eV} = 0.85252 \quad (15.143)$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

432. The system of claim 427, wherein the energies of each $\overset{3e}{C=C}$ bond of benzene are determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene.

433. The system of claim 427, wherein ethylene serves as a basis element for the $\overset{3e}{C=C}$ bonding of benzene wherein each of the six $\overset{3e}{C=C}$ bonds of benzene comprises $(0.75)(4)= 3$ electrons according to Eq. (15.142).

434. The system of claim 427, wherein the total energy of the bonds of the eighteen electrons of the $\overset{3e}{C=C}$ bonds of benzene, $E_T\left(C_6H_6,\overset{3e}{C=C}\right)$, is given by $(6)(0.75)$ times $E_{T+osc}(C=C)$ (Eq. (14.492)), the total energy of the $\overset{3e}{C=C}$-bond MO of benzene including the Doppler term, minus eighteen times $E\left(C,2sp^3\right)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the $\overset{3e}{C=C}$ bonds of bond order two.

435. The system of claim 427, wherein the total energy of the six $\overset{3e}{C=C}$ bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned} E_T\left(C_6H_6,\overset{3e}{C=C}\right) &= (6)(0.75)E_{T+osc}(C=C)-(6)(3)E\left(C,2sp^3\right) \\ &= (6)(0.75)(-66.05796\ eV)-18(-14.63489\ eV) \quad (15.144) \\ &= -297.26081\ eV-(-263.42798\ eV) \\ &= -33.83284\ eV \end{aligned}$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

436. The system of claim 427, wherein the results of benzene can be generalized to the class of aromatic and heterocyclic compounds. $E_{h\nu}$ of an aromatic bond is given by $E_T\left(H_2\right)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_2-type MO such that

$$\overline{E}_{osc} = n_1\left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1\left(-31.63536831\ eV\sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right) \qquad (15.145),$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

437. The system of claim 435, wherein the factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56).

438. The system of claim 437, wherein the multiplication of the total energy given by Eq. (15.55) by $f_1 = 0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_T\left(Group\right) = f_1\left(\begin{array}{l} E(basis\ energies) + E_T\left(atom - atom, msp^3.AO\right) \\ -31.63536831\ eV\sqrt{\dfrac{2\hbar\sqrt{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e}}{m_e c^2} + n_1\overline{E}_{Kvib} + c_3\frac{8\pi\mu_o\mu_B^2}{r^3} \end{array}\right) \qquad (15.146)$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

439. The system of claim 427, wherein the total bond energy of the aromatic group $E_D\left(Group\right)$ is the negative difference of the total energy of the group (Eq. (15.146)) and the

total energy of the starting species given by the sum of $c_4 E_{initial}\left(c_4\ AO/HO\right)$ and $c_5 E_{initial}\left(c_5\ AO/HO\right)$:

$$E_D(Group) = -\left(f_1 \left(\begin{array}{l} E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right) \\ -31.63536831\ eV \sqrt{\dfrac{2\hbar\sqrt{\dfrac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}}{m_e c^2}} + n_1 \bar{E}_{Kvib} + c_3 \dfrac{8\pi\mu_o \mu_B^2}{r^3} \end{array} \right) - \left(c_4 E_{initial}\left(AO/HO\right) + c_5 E_{initial}\left(c_5\ AO/HO\right) \right) \right)$$

(15.147), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

440. The system of claim 427, wherein benzene is considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms, energy components of V_e, V_p, T, V_m, and E_T are the same as those of the hydrogen carbide radical, except that $E_T\left(C=C, 2sp^3\right) = -1.13379\ eV$ (Eq. (14.247)) is subtracted from $E_T(CH)$ of Eq. (13.495) to match the energy of each $C-H$-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

441. The system of claim 440, wherein in the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T\left(atom-atom, msp^3.AO\right) = -1.13379\ eV$ wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to ± 10%, if desired.

442. The system of claim 440, wherein the total energy of the benzene $C-H$-bond MO, $E_{T_{benzene}}\left(C-H\right)$, given by Eq. (14.467) is the sum of $0.5E_T\left(C=C, 2sp^3\right)$, the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the

formation of the corresponding $C\overset{3e}{=}C$-bond MO (Eq. (14.247)), and $E_{T_{benzene}}(CH)$, the σ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_1 = 1$ and $E_T(atom-atom, msp^3.AO) = \frac{-1.13379\ eV}{2}$, wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

443. The system of claim 442, wherein the energy contribution to the single aromatic CH bond is one half that of the $C\overset{3e}{=}C$ double bond contribution, which matches the energies of the CH and $C\overset{3e}{=}C$ aromatic groups, conserves the electron number with the equivalent charge density as that of $s = 1$ in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule.

444. The system of claim 443, wherein the breakage of the aromatic $C\overset{3e}{=}C$ bonds to give CH groups creates unpaired electrons in these fragments that corresponds to $c_3 = 1$ in Eq. (15.56) with E_{mag} given by Eq. (15.58).

445. The system of claim 444, wherein each of the $C-H$ bonds of benzene comprises two electrons according to Eq. (14.439).

446. The system of claim 445, wherein from the energy of each $C-H$ bond, $-E_{D_{benzene}}(^{12}CH)$ (Eq. (14.477)), the total energy of the twelve electrons of the six $C-H$ bonds of benzene, $E_T(C_6H_6, C-H)$, given by Eq. (14.494) is

$$E_T(C_6H_6, C-H) = (6)(-E_{D_{benzene}}(^{12}CH)) = 6(-3.90454\ eV) = -23.42724\ eV$$

(15.148), wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

447. The system of claim 440, wherein the total bond dissociation energy of benzene, $E_D\left(C_6H_6\right)$, given by Eq. (14.495) is the negative sum of $E_T\left(C_6H_6,C\overset{3e}{=}C\right)$ (Eq. (14.493)) and $E_T\left(C_6H_6,C-H\right)$ (Eq. (14.494)):

$$\begin{aligned} E_D\left(C_6H_6\right) &= -\left(E_T\left(C_6H_6,C\overset{3e}{=}C\right)+E_T\left(C_6H_6,C-H\right)\right) \\ &= -\left(\left(-33.83284\ eV\right)+\left(-23.42724\ eV\right)\right) \\ &= 57.2601\ eV \end{aligned} \qquad (15.149)$$

wherein the calculated and measured values and constants recited in the equations herein can be adjusted, for example, up to $\pm$ 10%, if desired.

448. The system of claim 447, wherein using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

449. A system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising:

processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie to produce at least one Maxwellian solution; and

an output means for outputting the Maxwellian solution.

450. The system of claim 449, further comprising a data transfer system for inputting numerical data into or out of a computational components and storage components of the main system.

451. The system of claim 449, further comprising a spreadsheet containing solutions of the bond parameters with output in a standard spreadsheet format.

452. The system of claim 451, further comprising a data-handling program to transfer data from the spreadsheets into the main program.

453. The system of claim 449, wherein output may be at least one of graphical, simulation, text, and numerical data.

454. The system of claim 453, wherein the output may be the calculation of at least one of: (1) a bond distance between two of the atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two of the atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration

455. The system of claim 449, wherein the charge, current, energy, and geometrical parameters are output to be inputs to other programs that can be used in further applications.

456. The system of claim 455, wherein the data of heats of formation can be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways.

457. The system of claim 456, wherein novel composition of matters can be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

458. The system of claim 456, wherein the charge and current density functions can be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species.

459. The system of claim 458, wherein finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index.

460. The system of claim 449, wherein the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization.

461. The system of claim 449, wherein the data can be input into other programs of the system, which calculate thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

462. A method of using any of the systems or compositions of matter of claims 1-461.

463. A use of any system or composition of matter of claims 1-461.

Fig.1

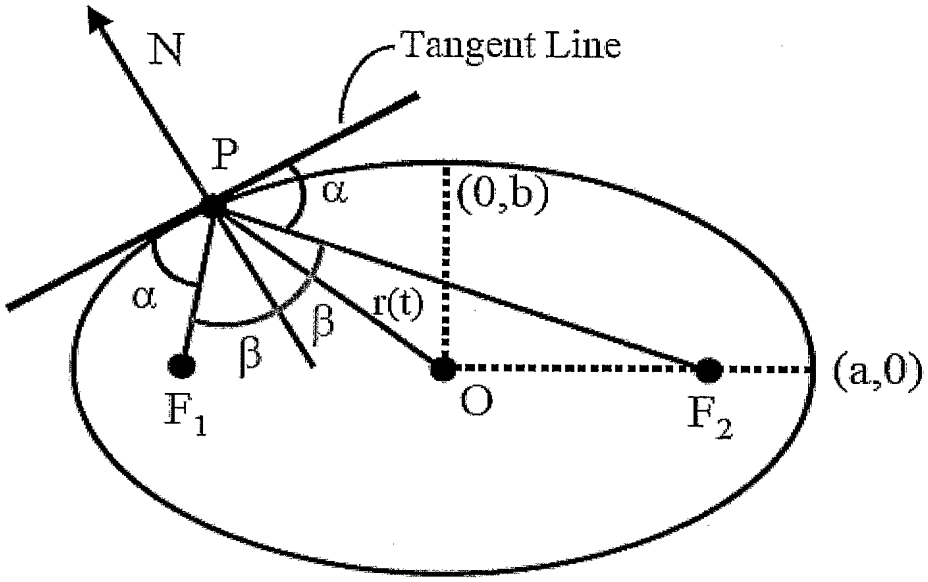


Fig.2

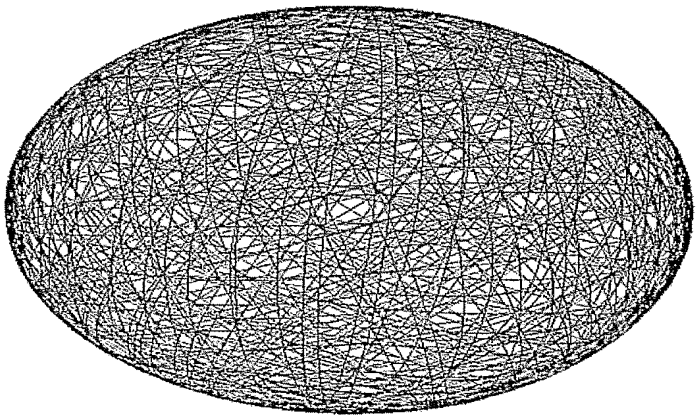


Fig.3

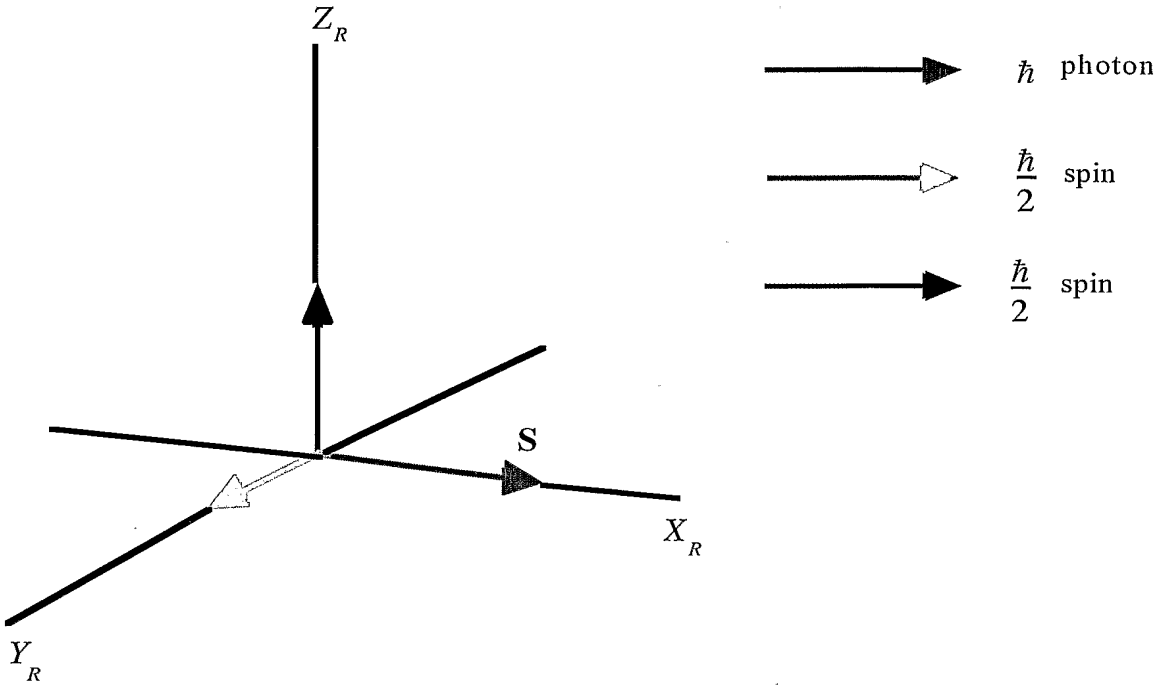


Fig.4

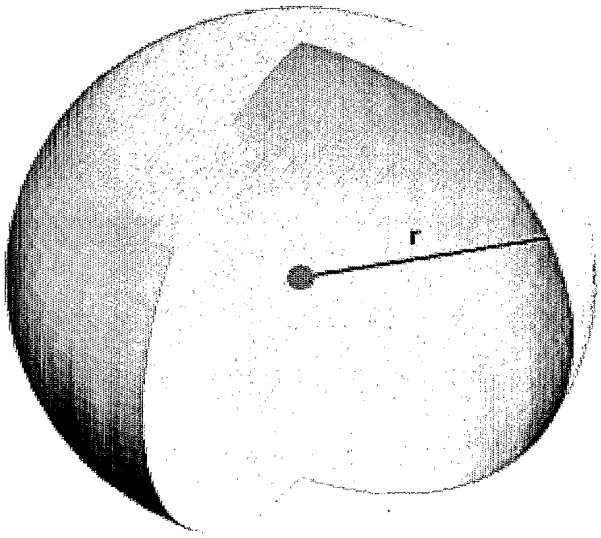
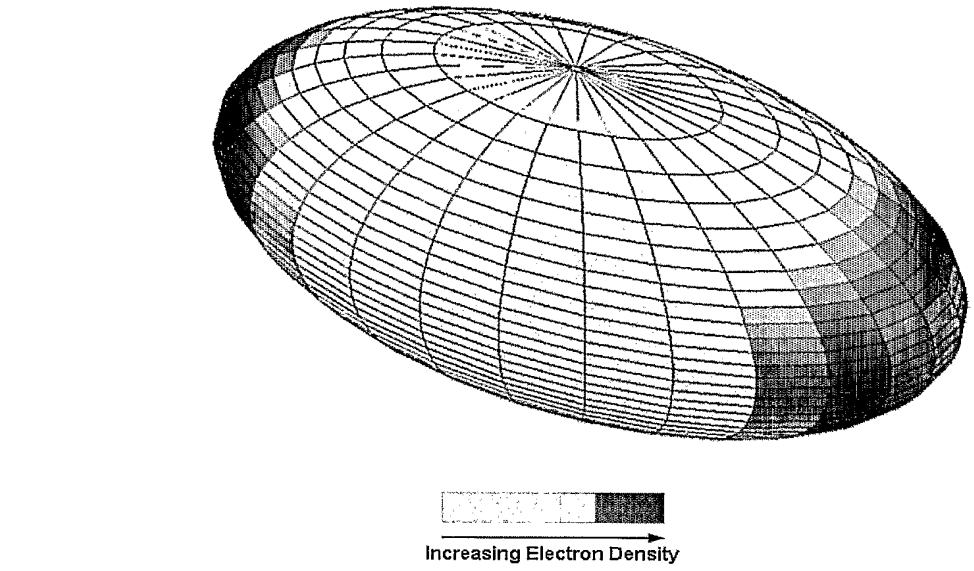
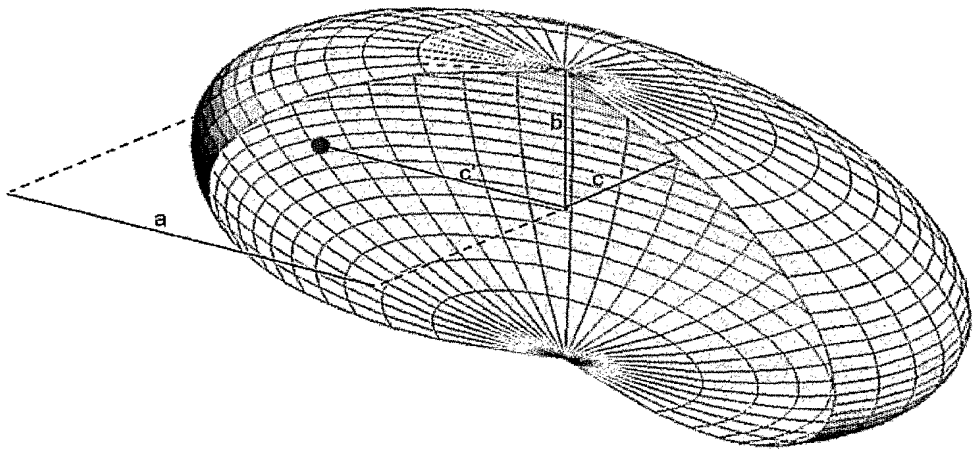


Fig.5



A



B

Fig. 6

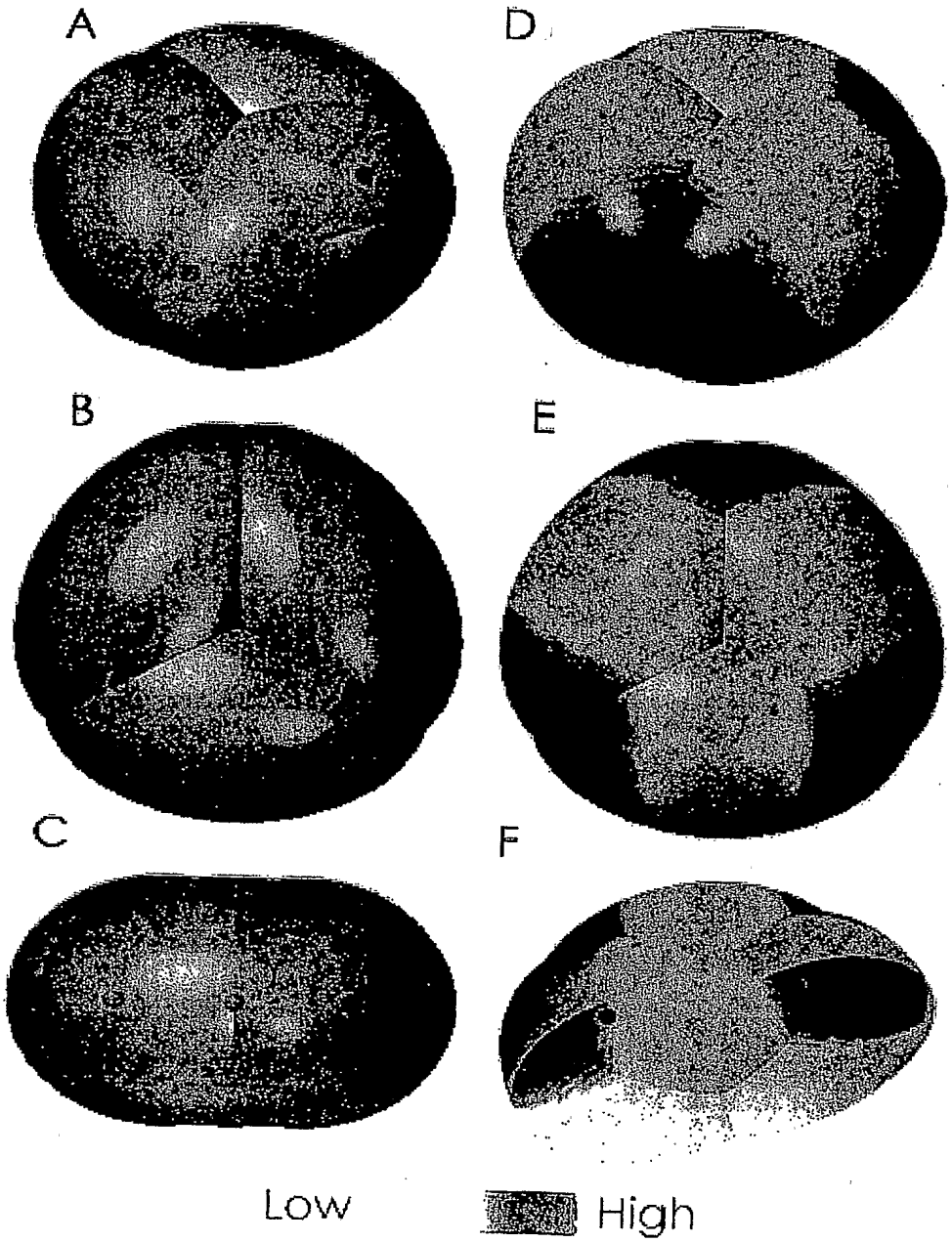


Fig.7

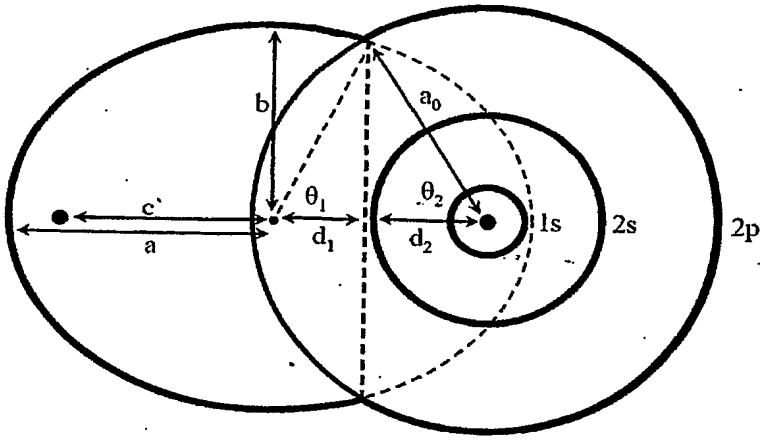


Fig.8

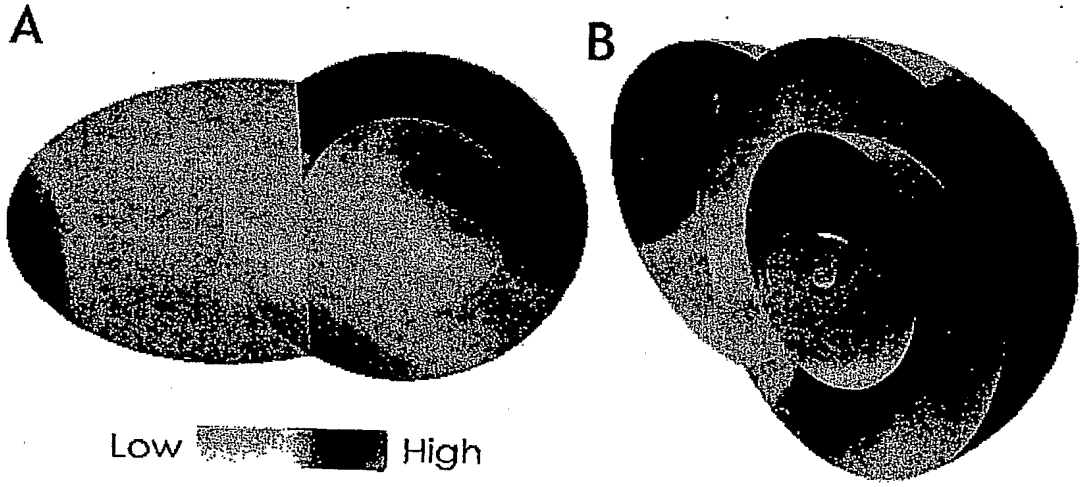


Fig.9

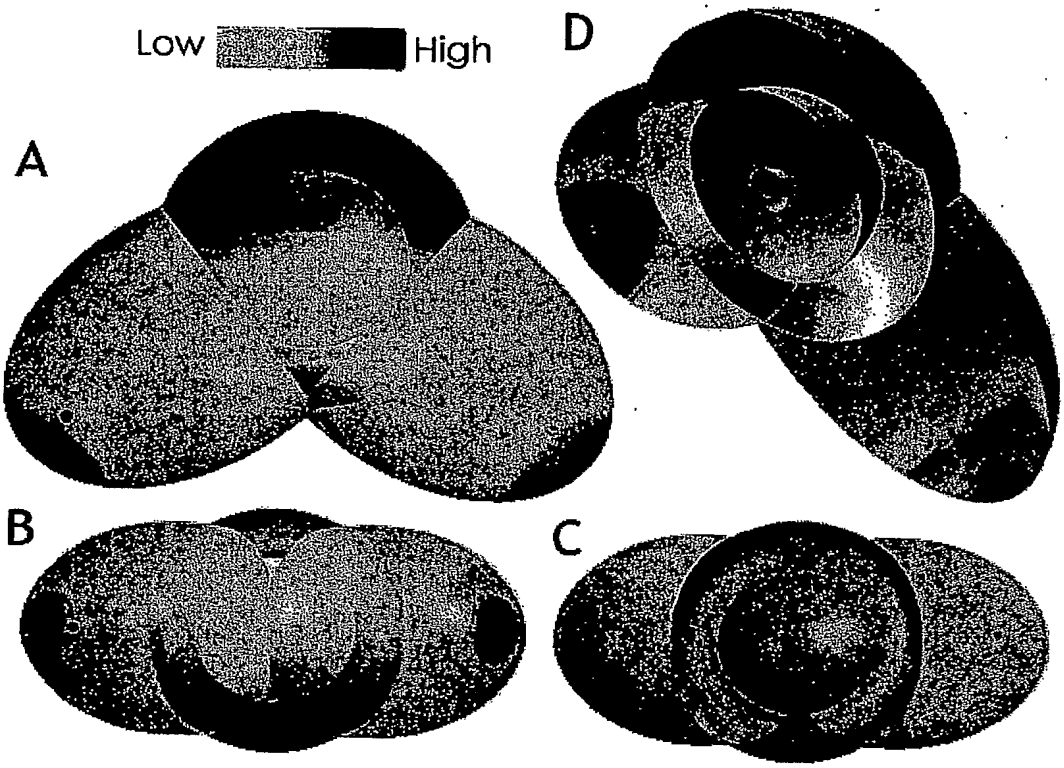


Fig.10

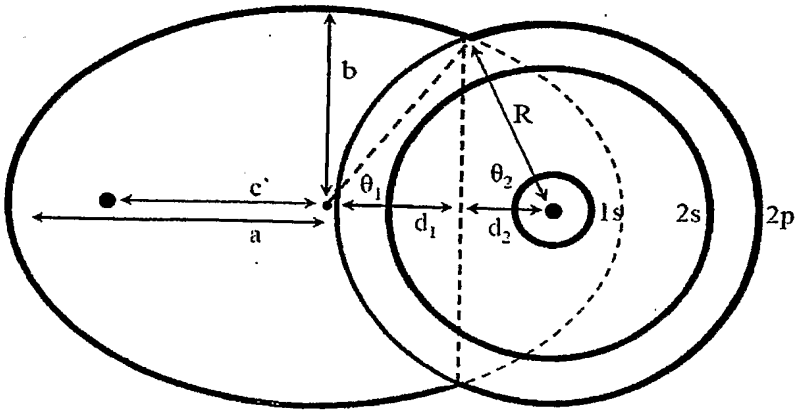


Fig.11

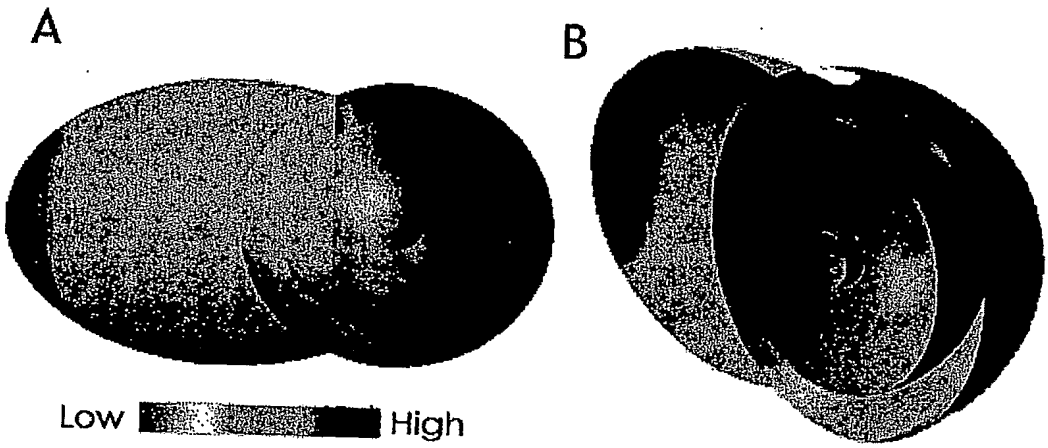


Fig.12

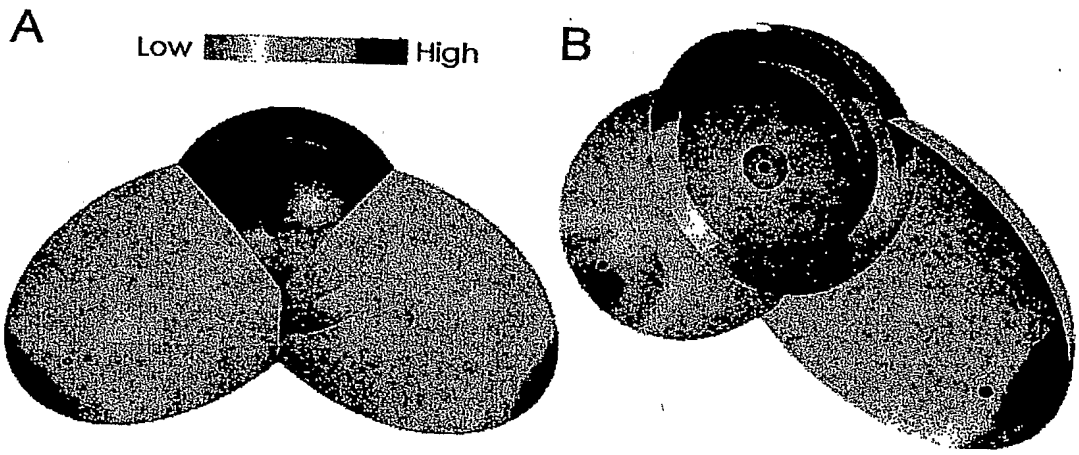


Fig. 13

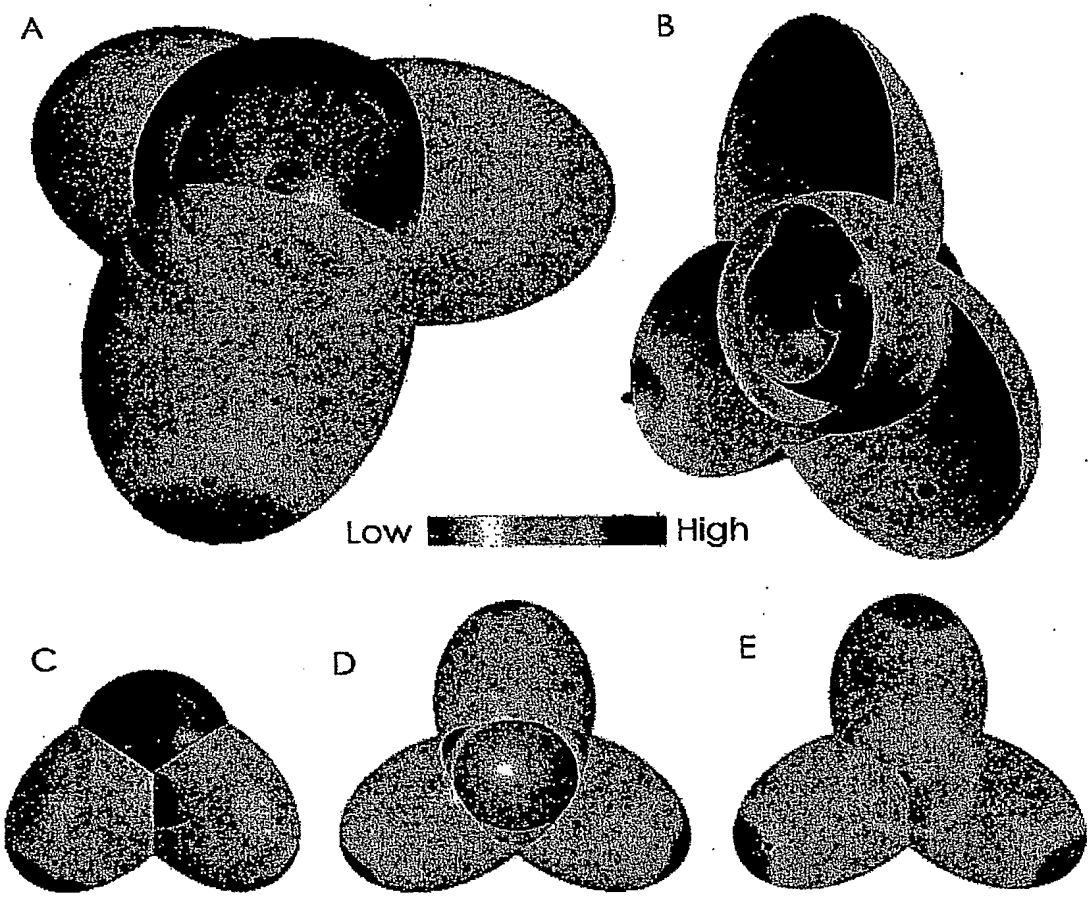


Fig.14

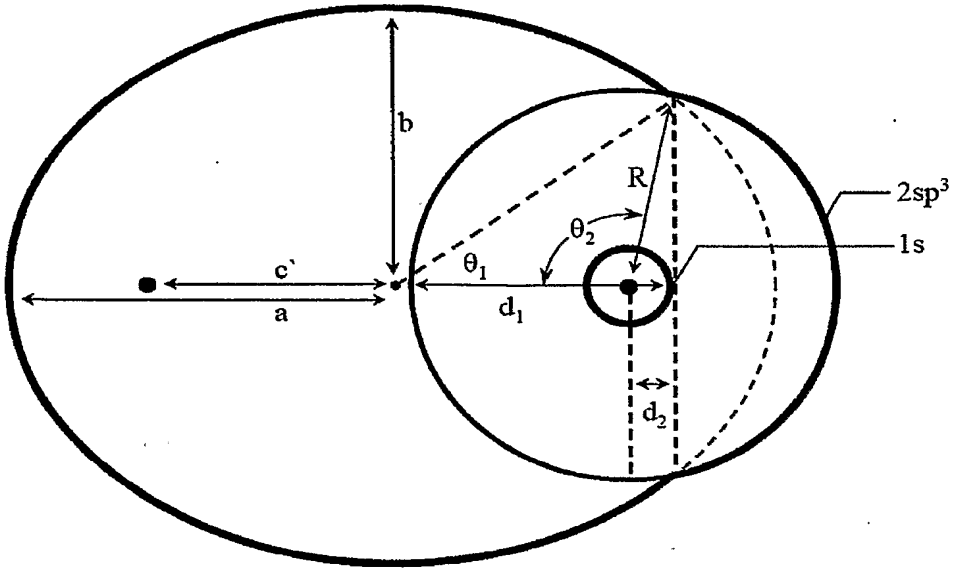


Fig.15

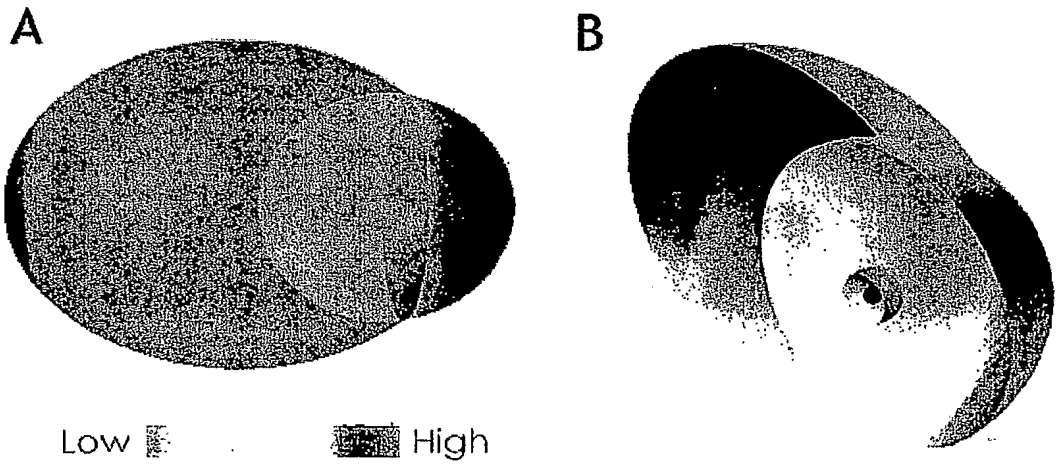


Fig.16

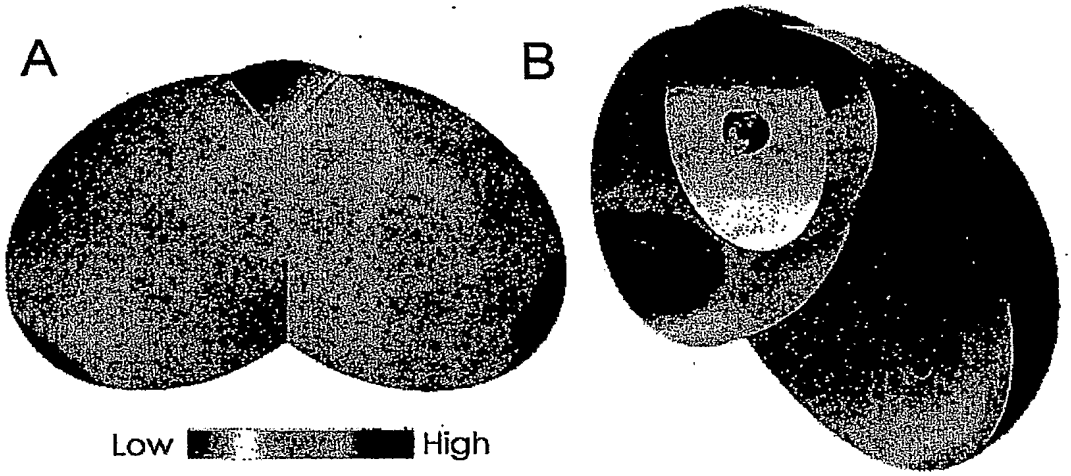


Fig.17

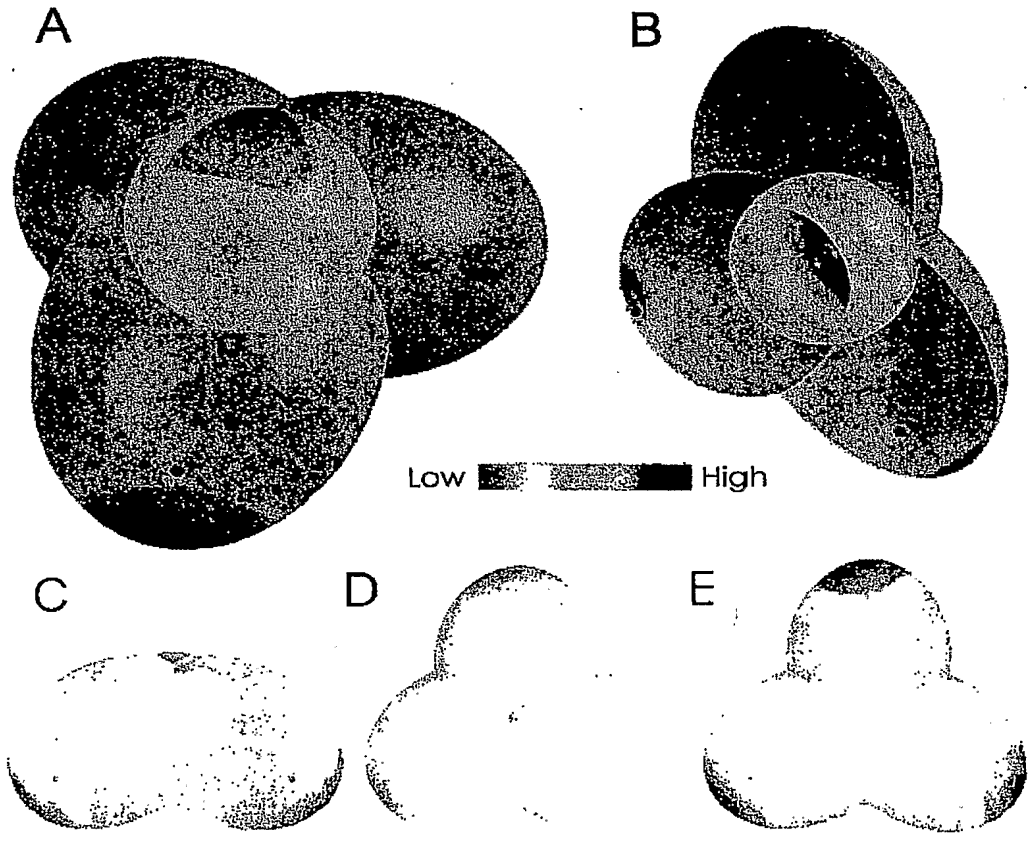


Fig.18

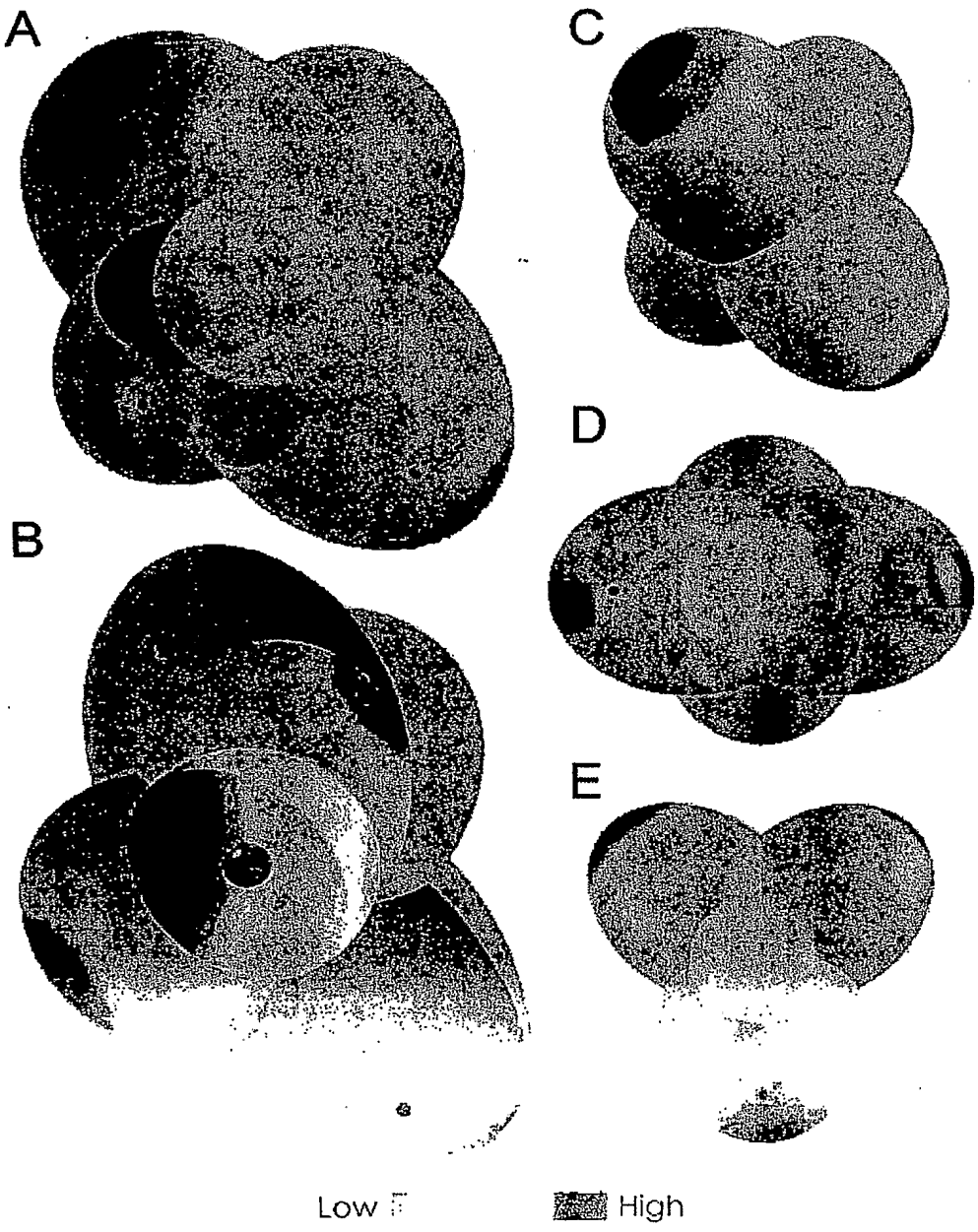


Fig.19

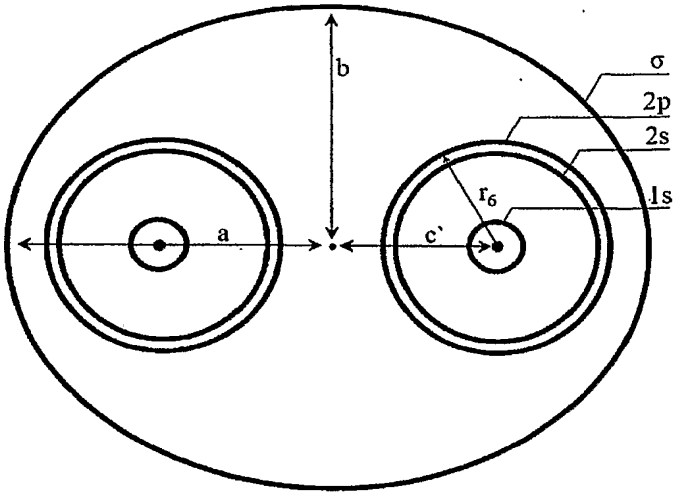


Fig.20

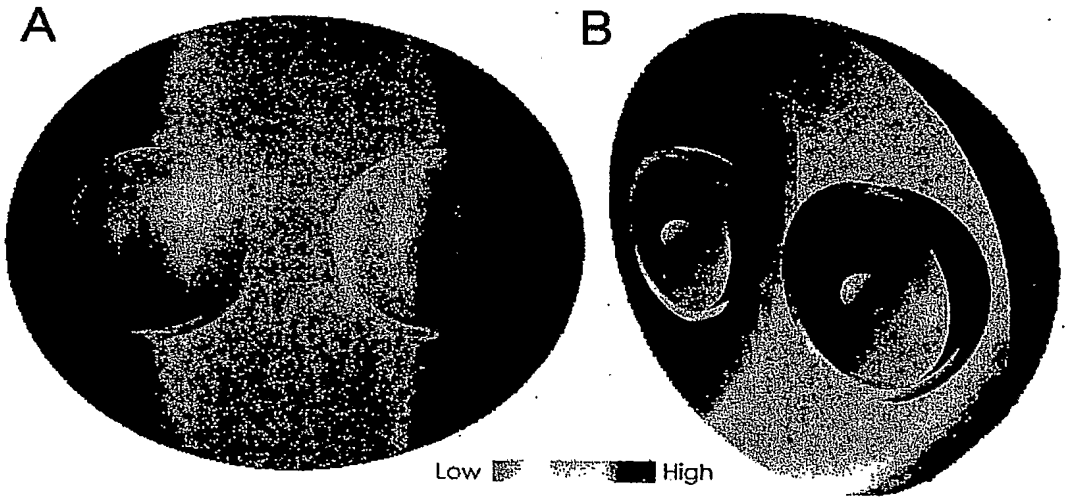


Fig.21

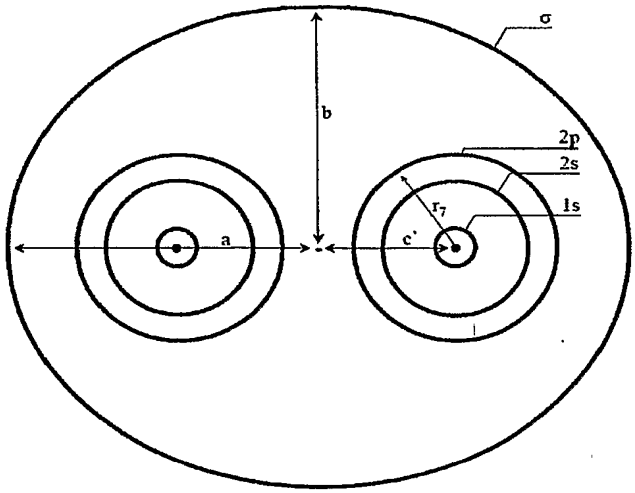


Fig.22

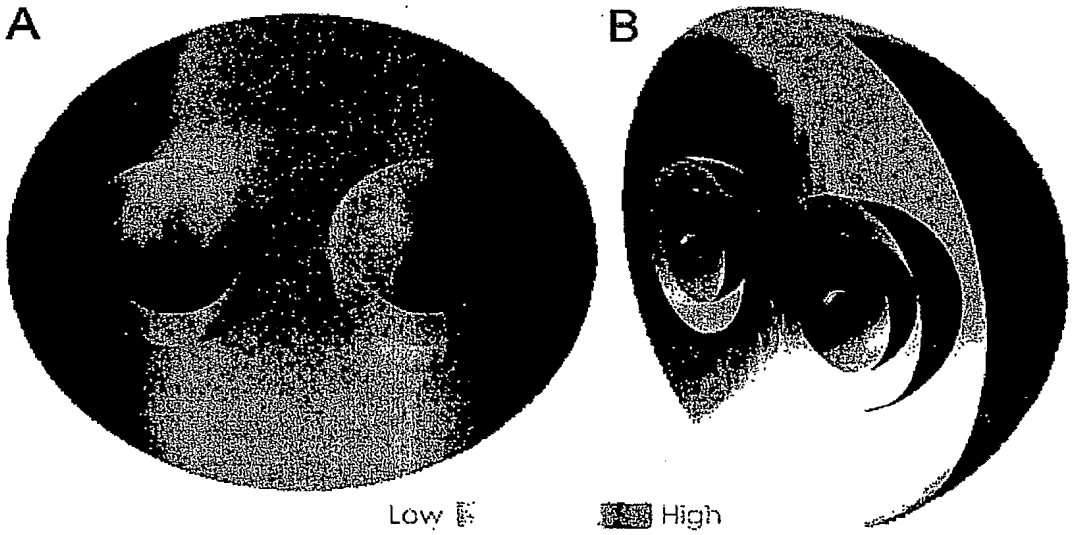


Fig.23

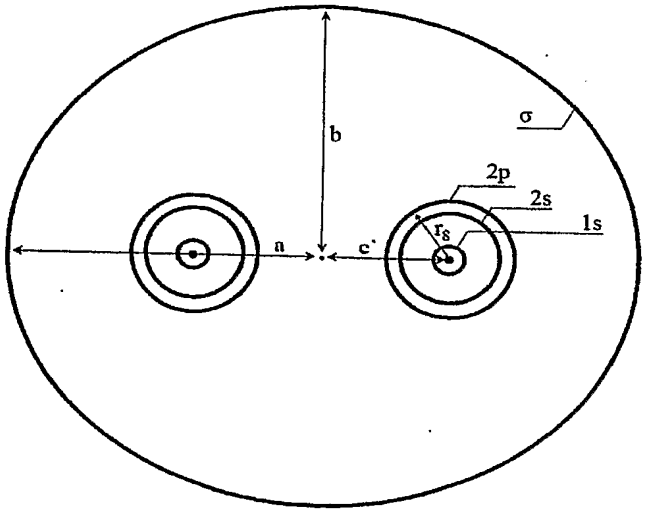


Fig.24

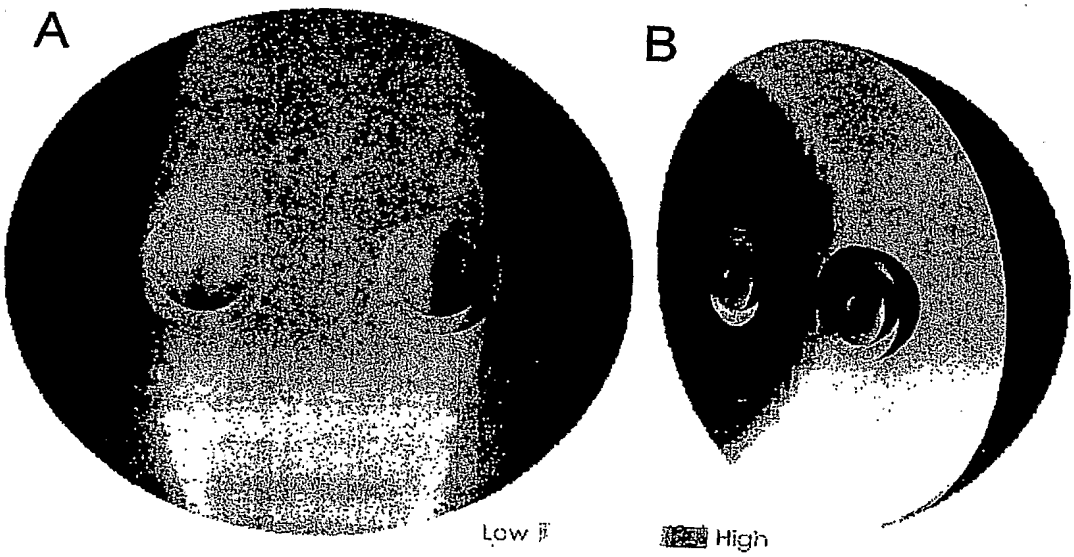


Fig.25

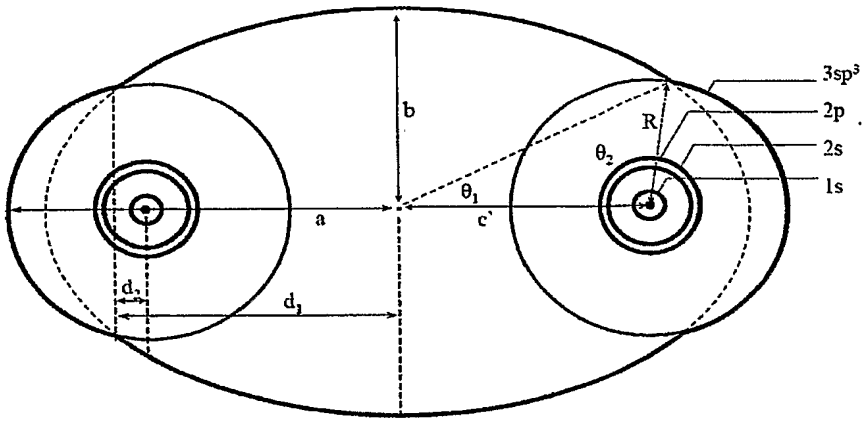


Fig.26

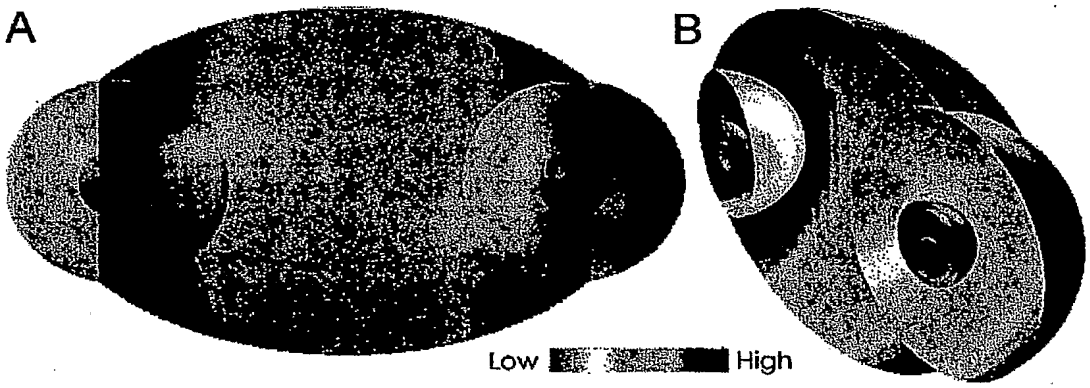


Fig.27

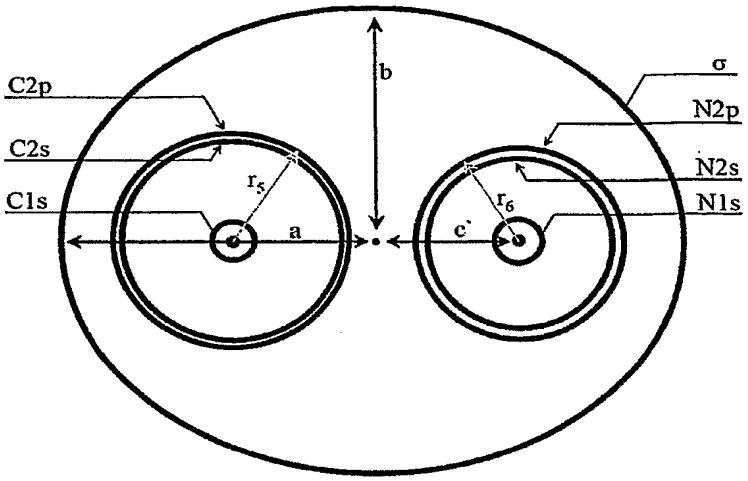


Fig.28

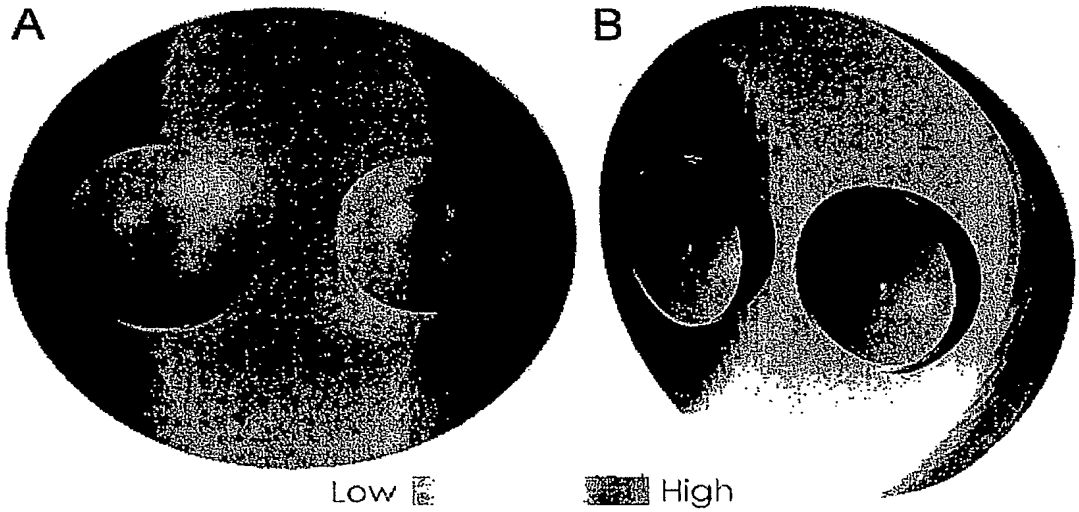


Fig.29

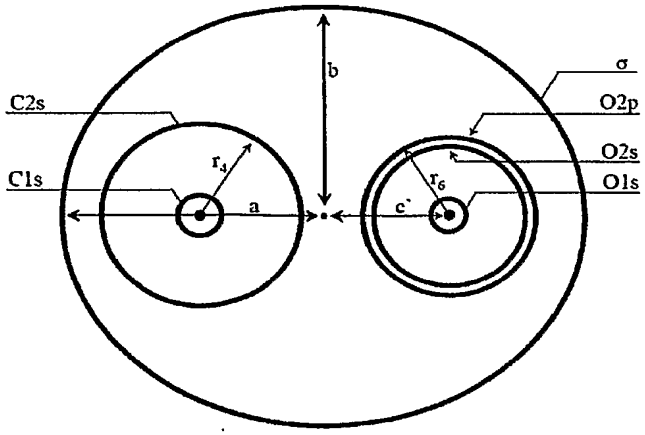


Fig.30

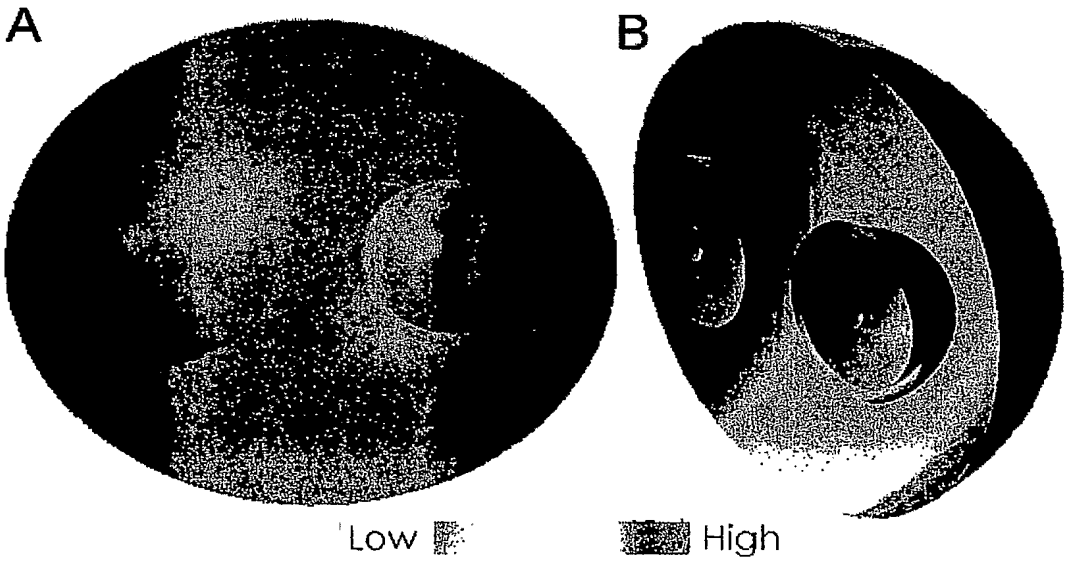


Fig.31

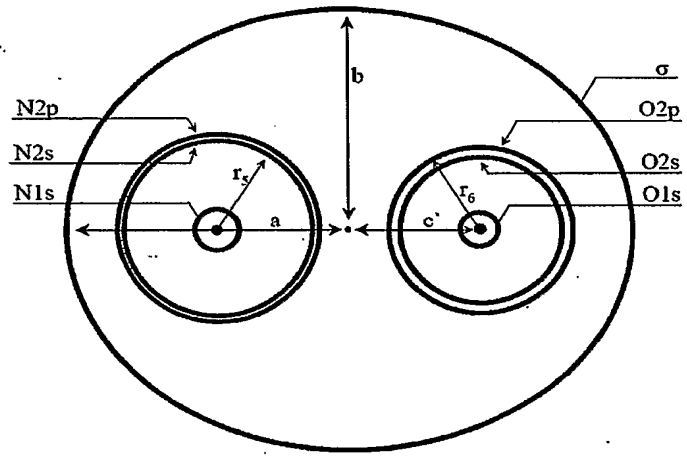


Fig.32

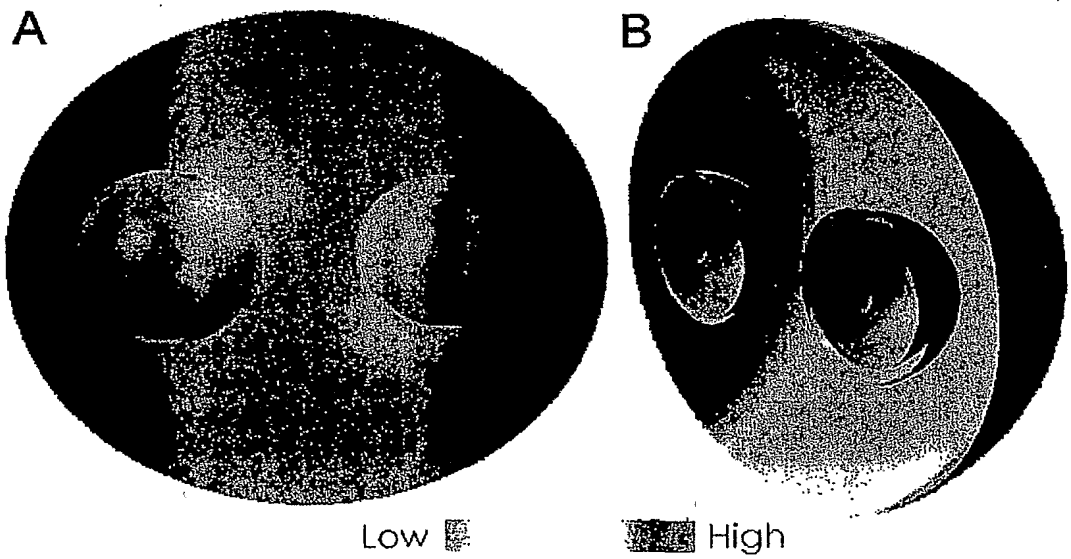


Fig.33

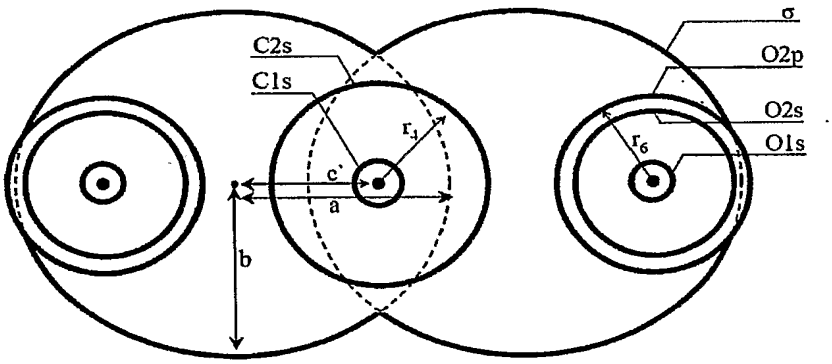


Fig.34

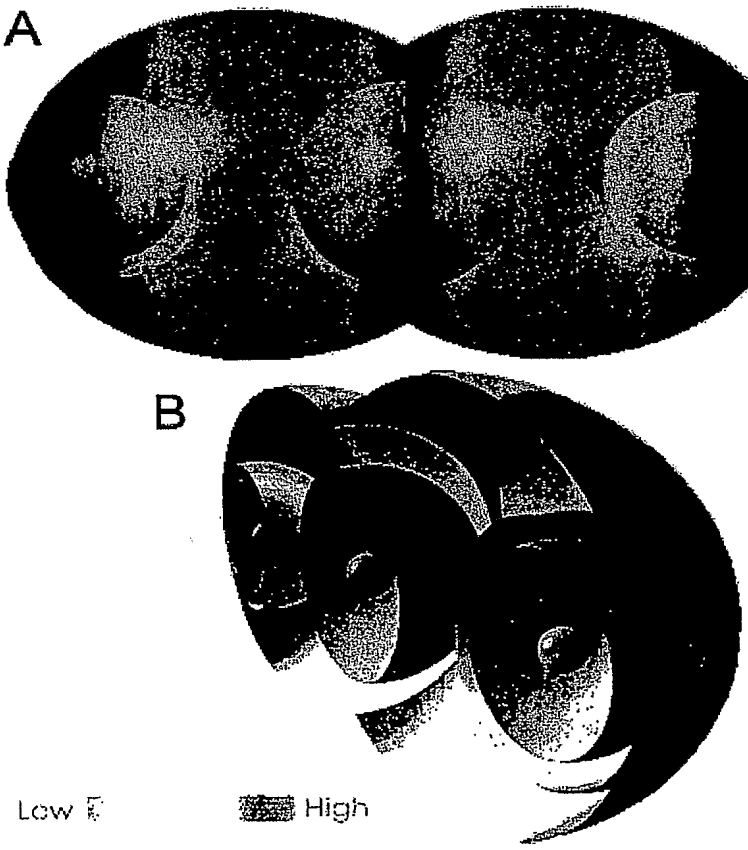


Fig.35

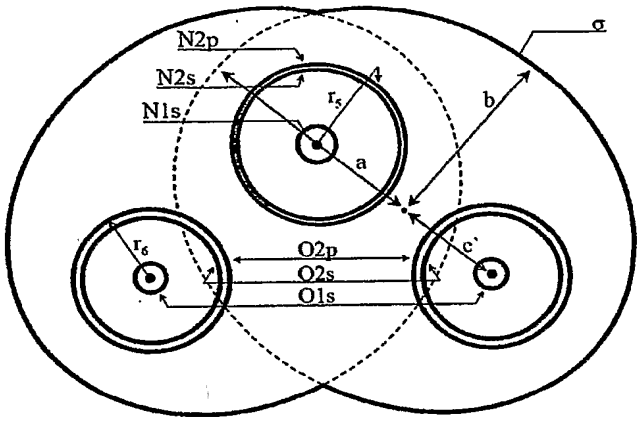


Fig.36

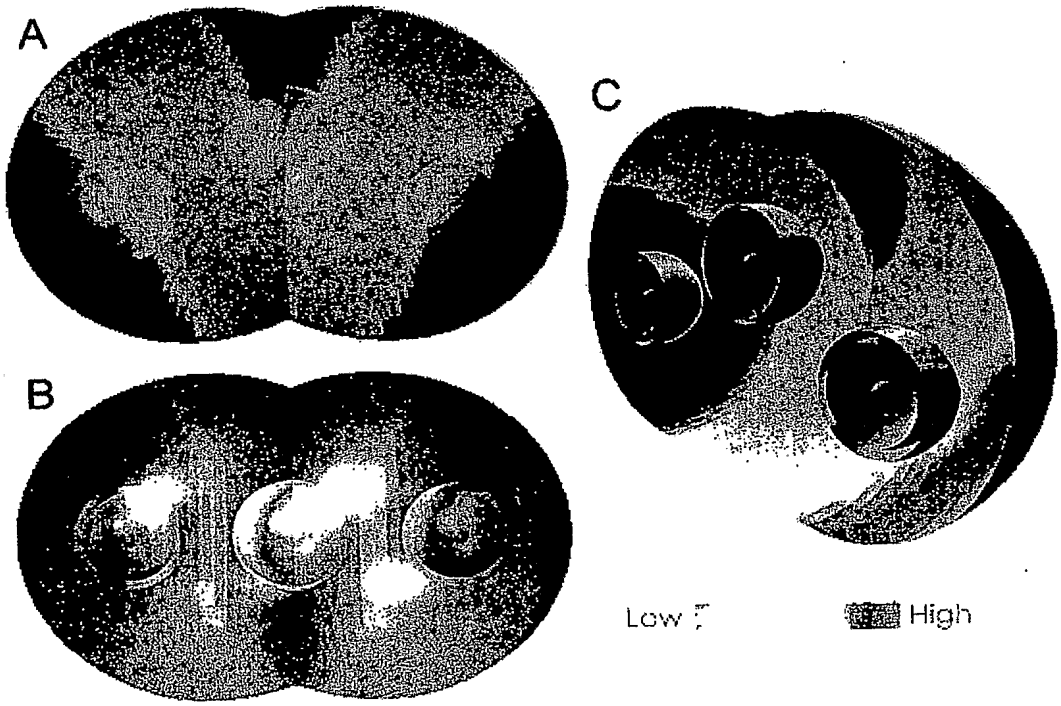


Fig.37

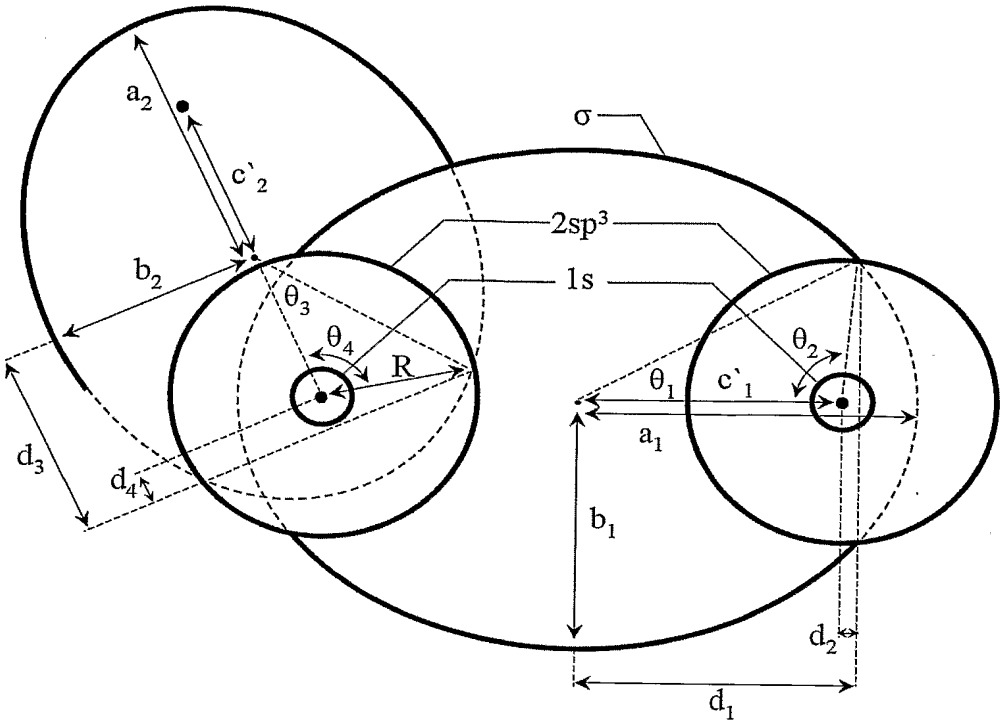

a2
c`2
σ
2sp3
b2
1s
θ3
θ4
R
θ2
θ1
c`1
a1
d3
d4
b1
d2
d1

Fig.38

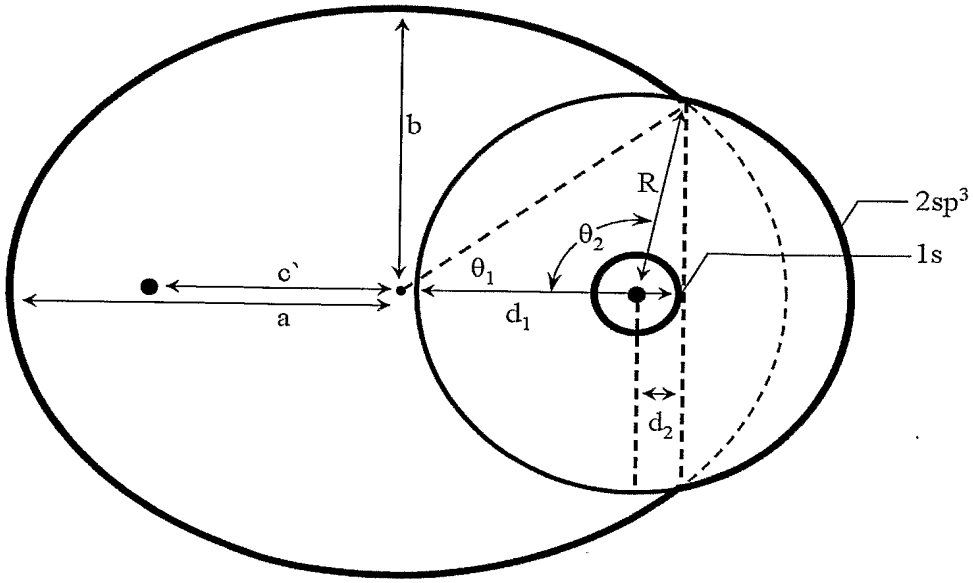

b
R
2sp3
θ2
1s
c`
θ1
a
d1
d2

Fig.39

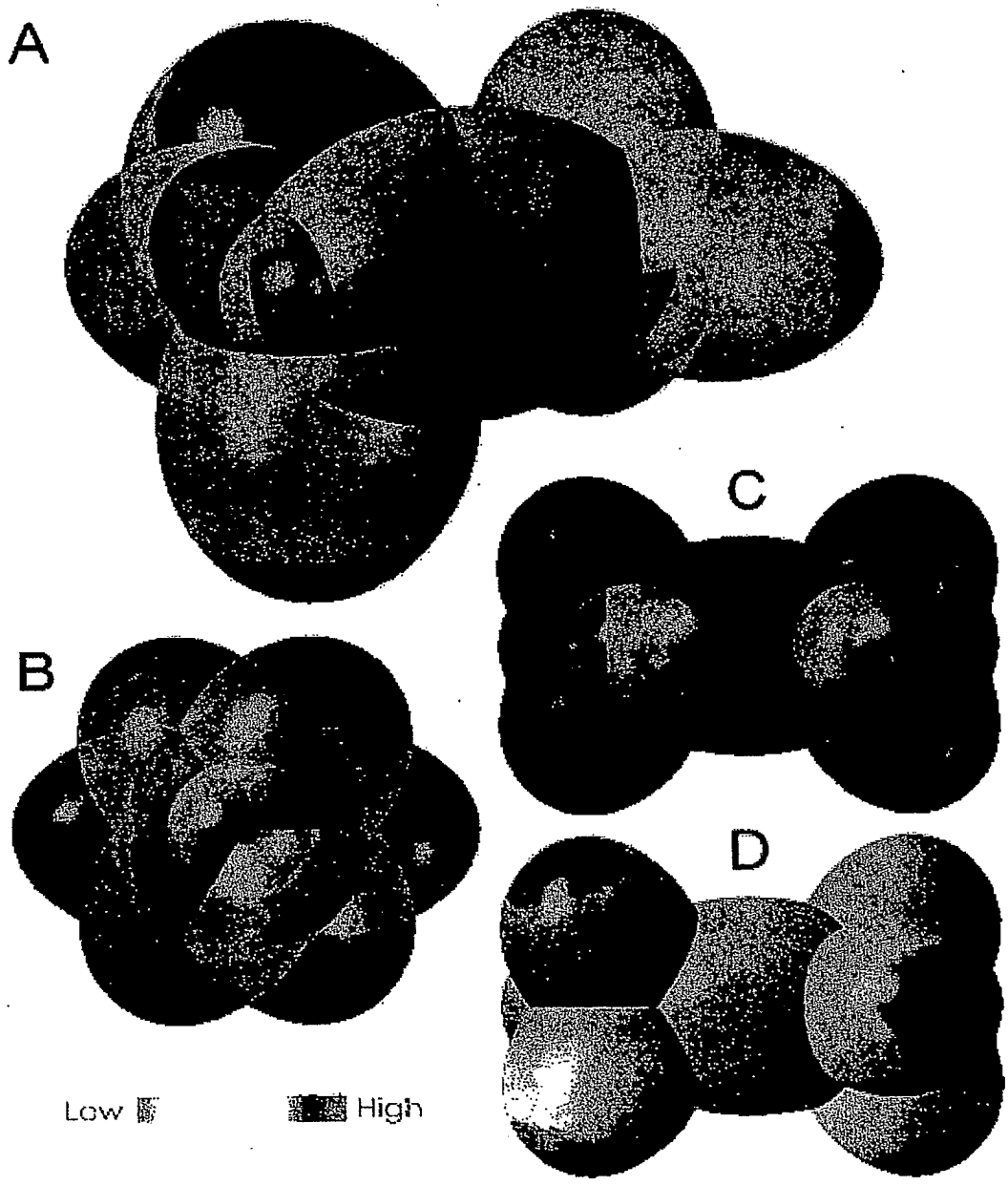


Fig.40

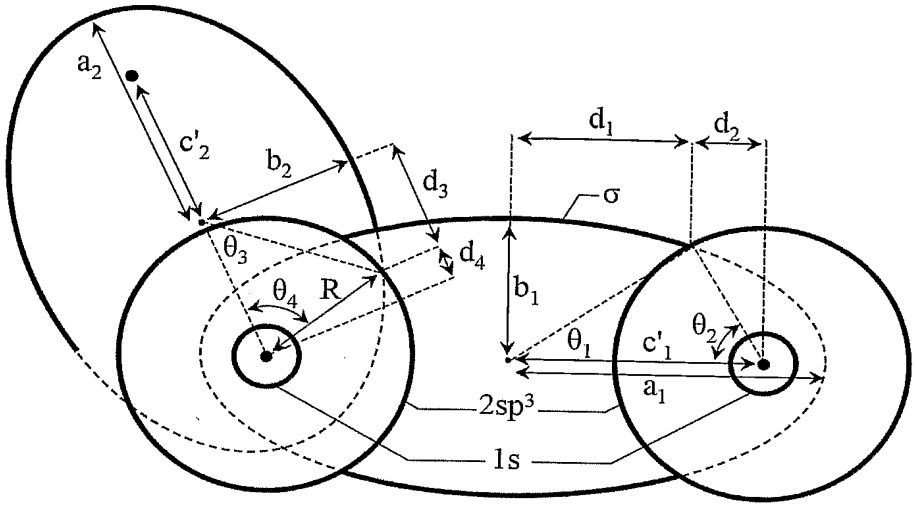

a2
c'2
b2
d3
d1
d2
σ
θ3
d4
θ4
R
b1
θ1
c'1
θ2
a1
2sp3
1s

Fig.41

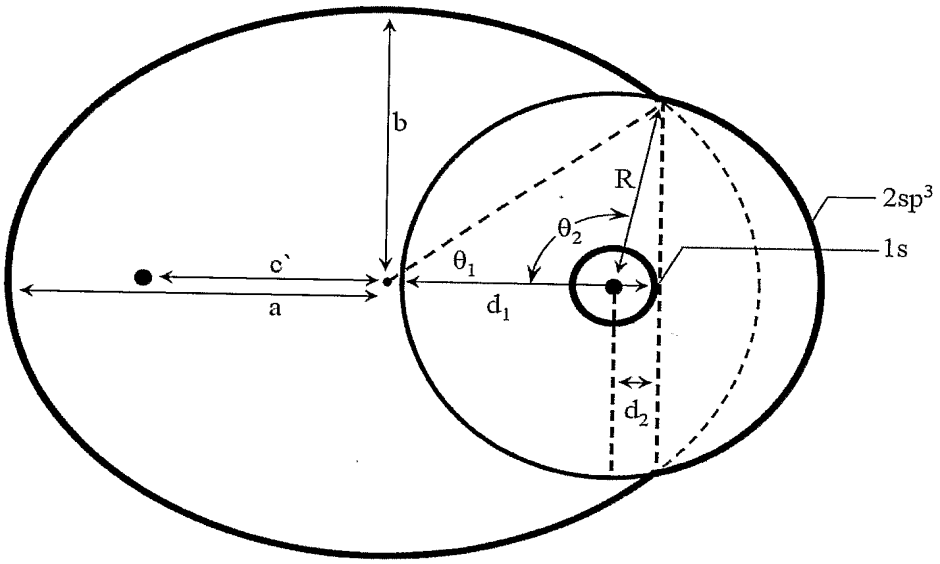

b
R
2sp3
θ2
1s
c`
θ1
a
d1
d2

Fig.42

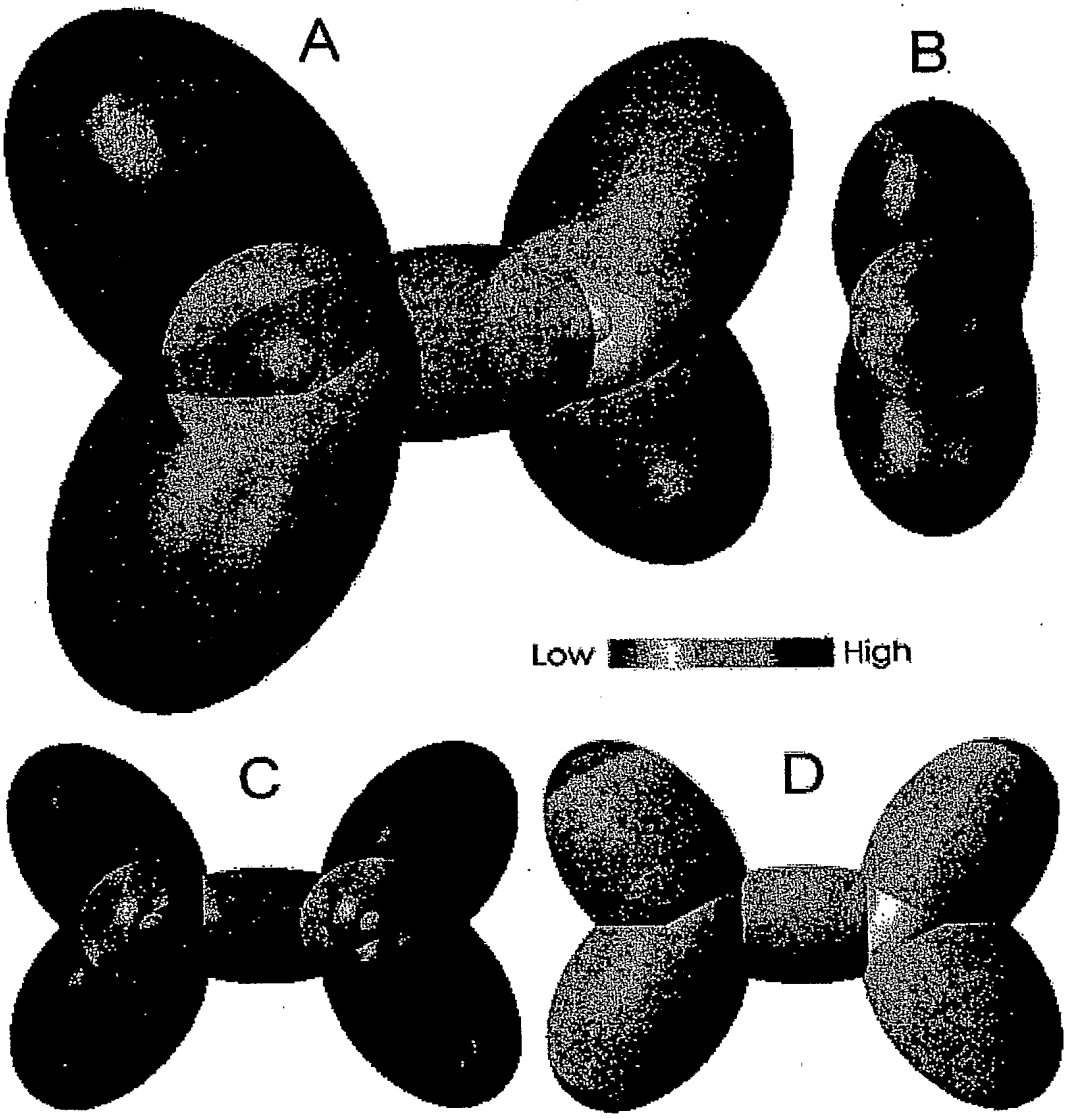


Fig.43

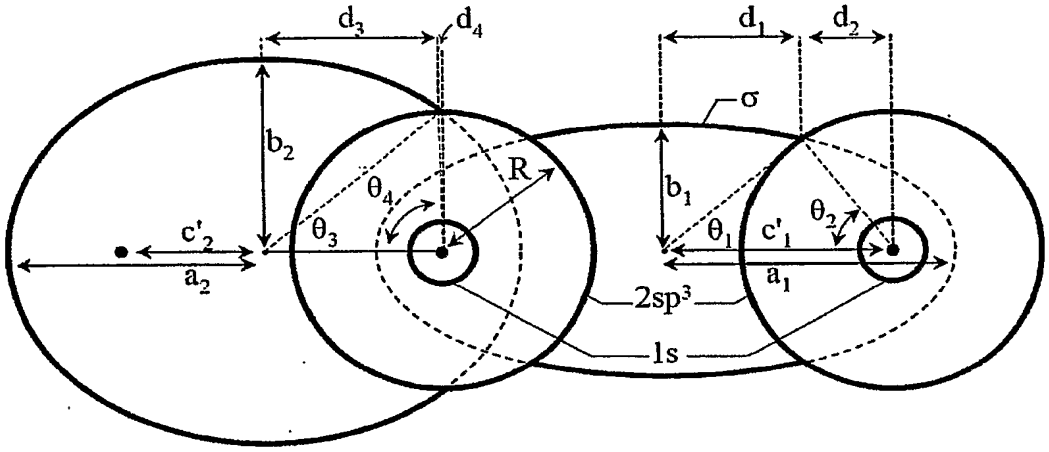


Fig.44

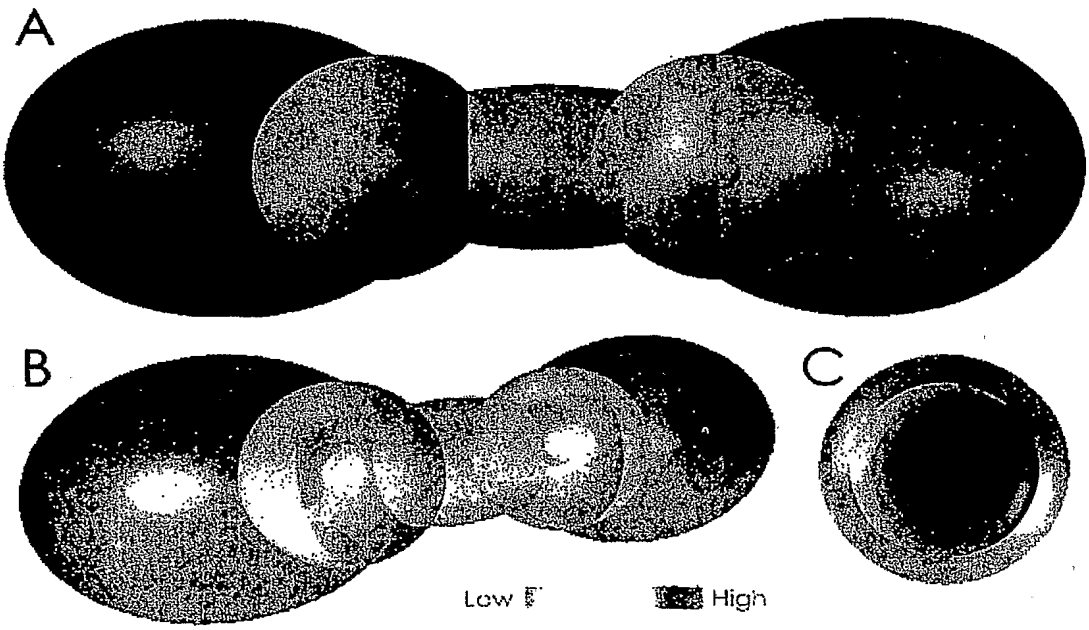


Fig.45

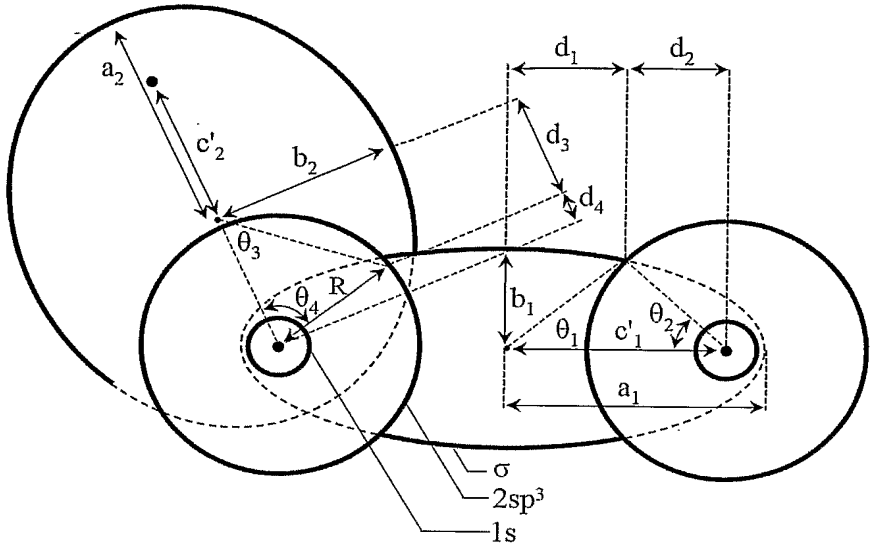

a2
c'2
b2
θ3
θ4
R
d1
d2
d3
d4
b1
θ1
c'1
θ2
a1
σ
2sp3
1s

Fig.46

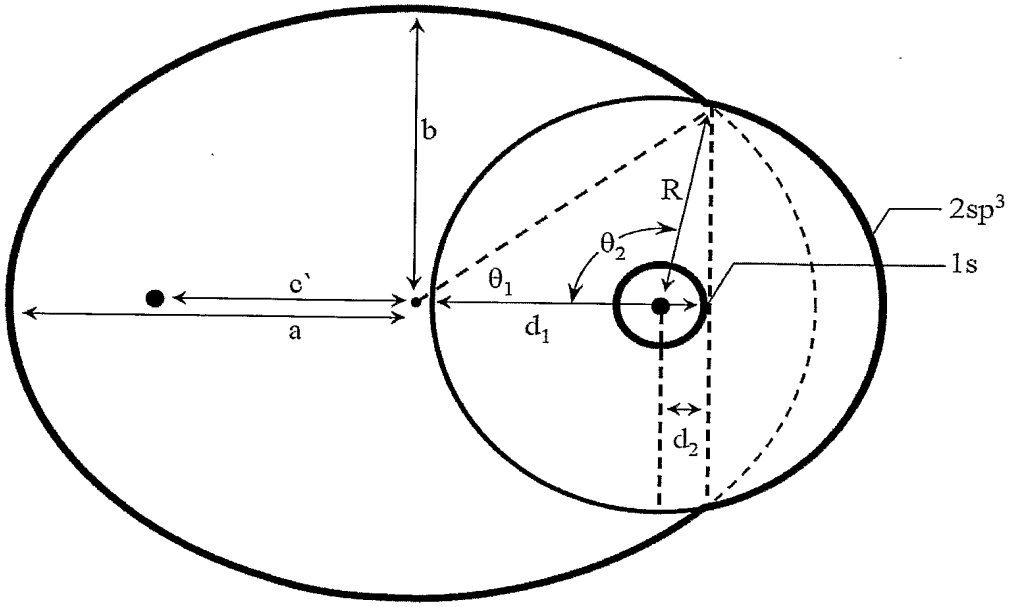

b
c`
a
θ1
θ2
R
d1
d2
2sp3
1s

Fig.47

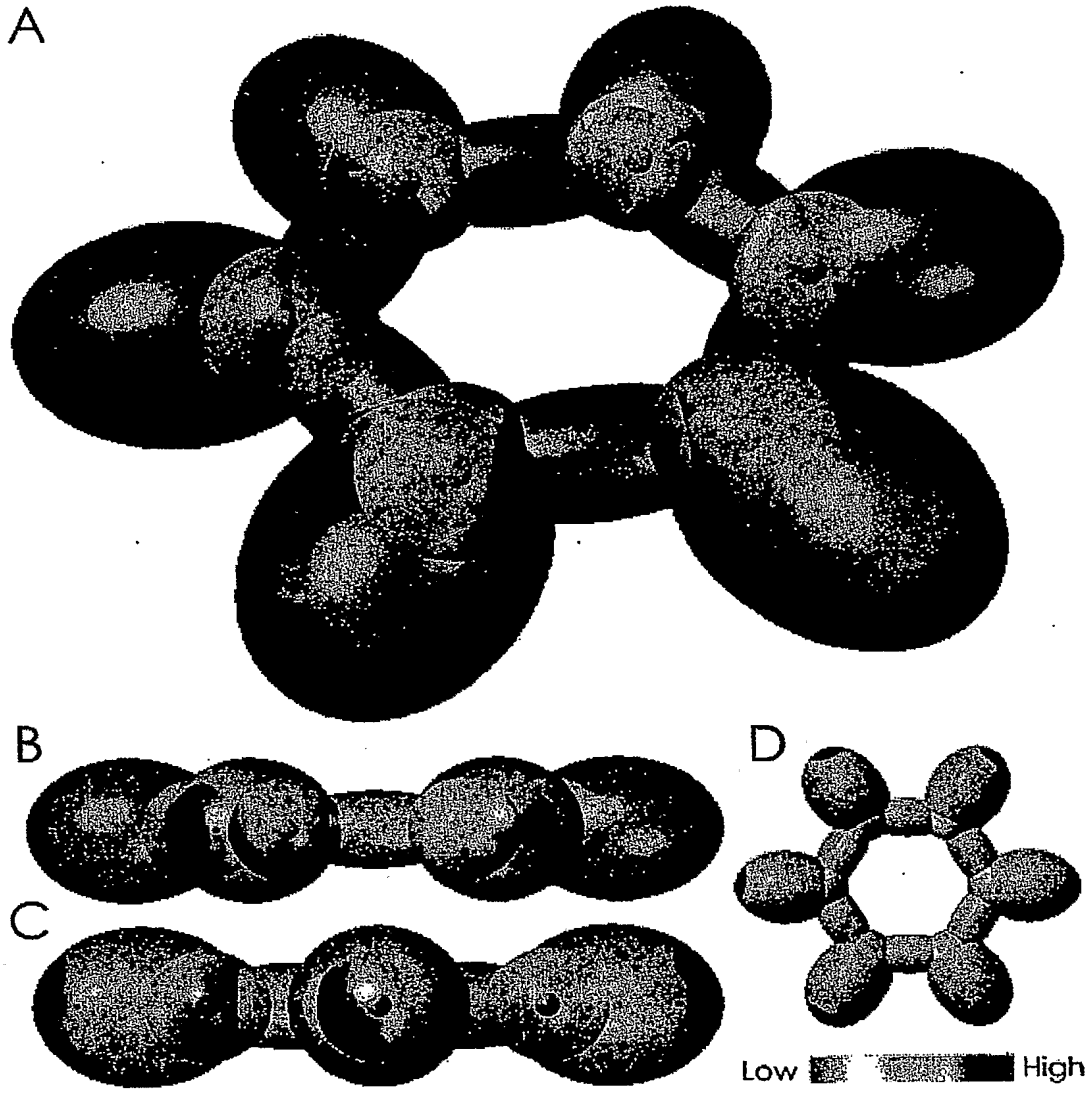


Fig.48

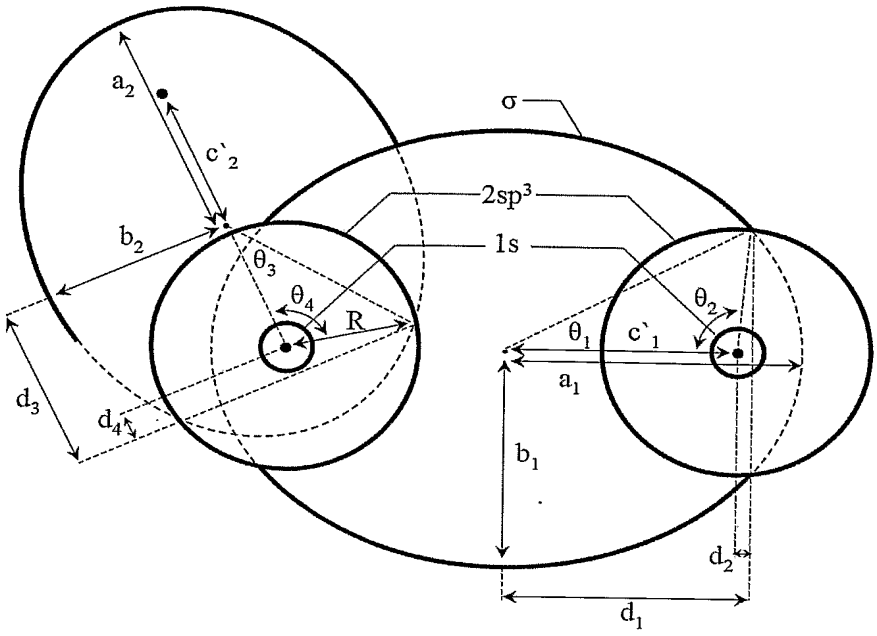

a2
c`2
σ
2sp3
b2
1s
θ3
θ4
R
θ2
θ1
c`1
a1
d3
d4
b1
d2
d1

Fig.49

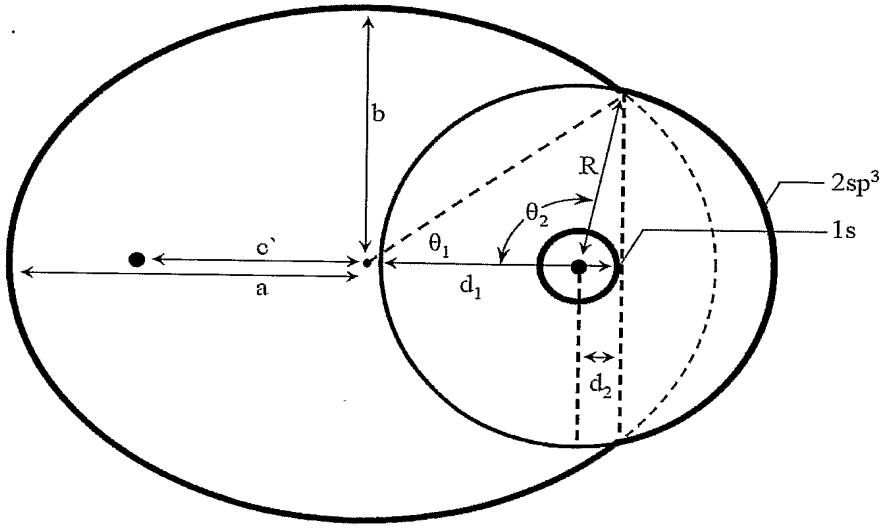

b
R
2sp3
θ2
1s
c`
θ1
a
d1
d2

Fig.50

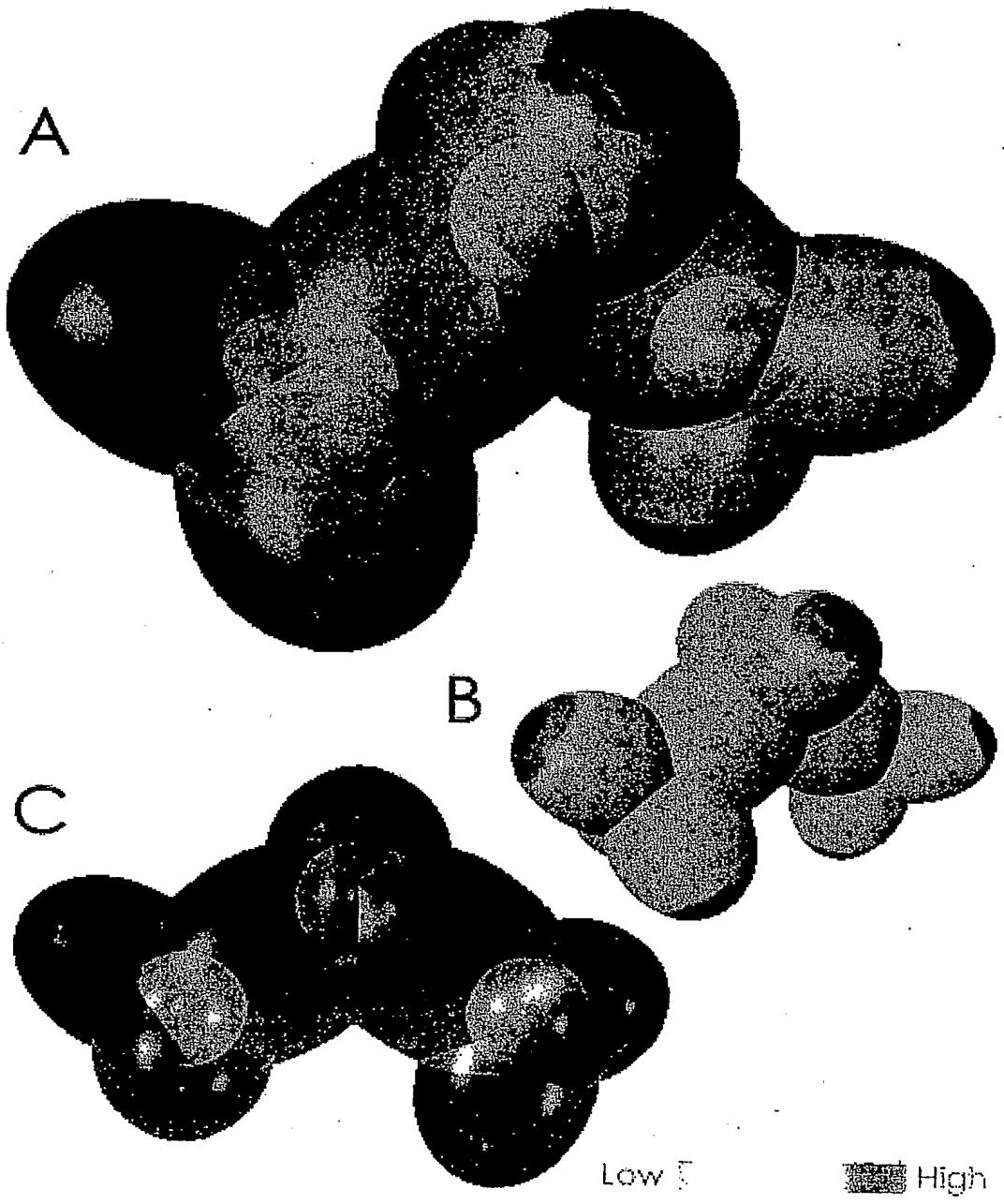


Fig.51

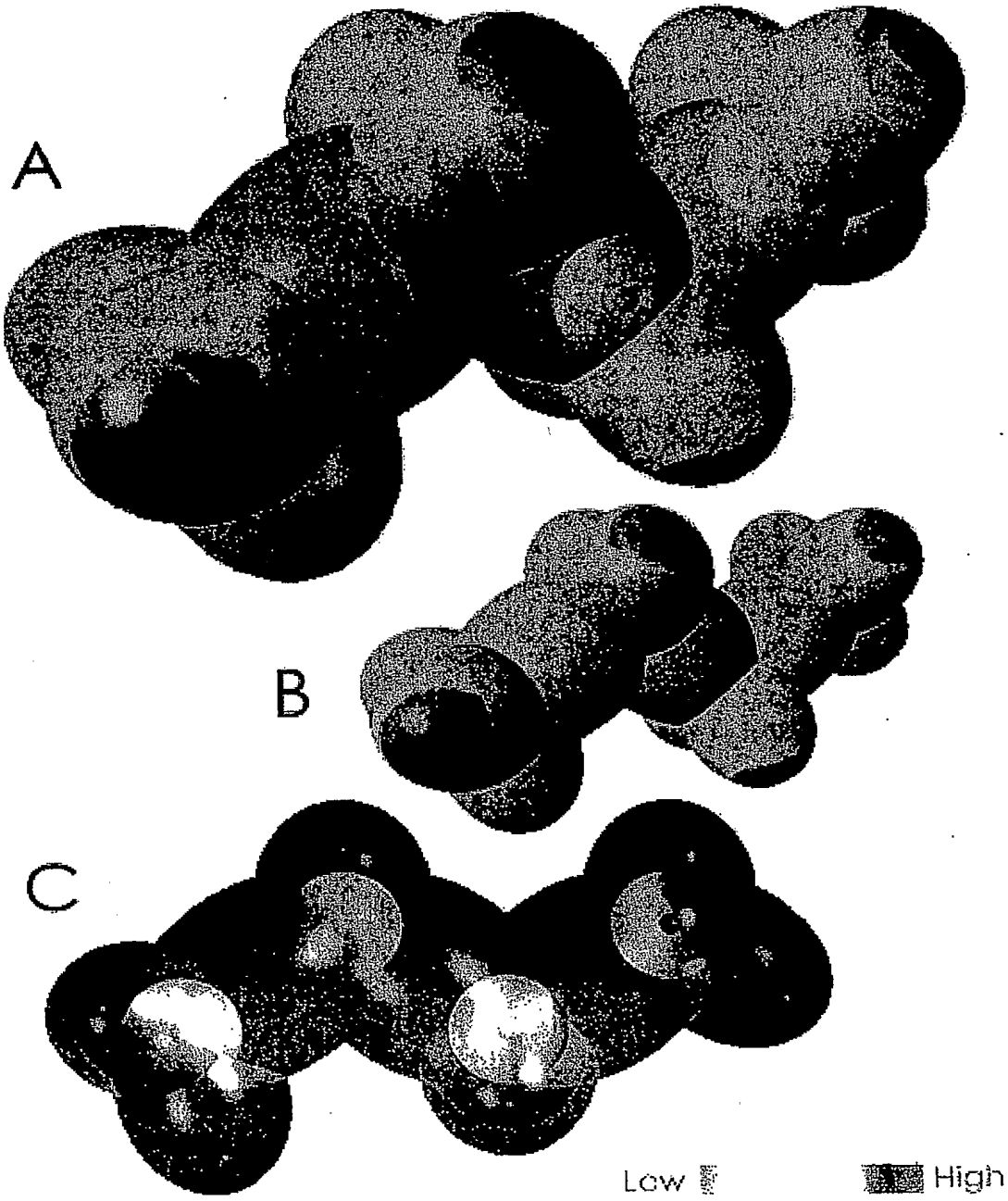


Fig.52

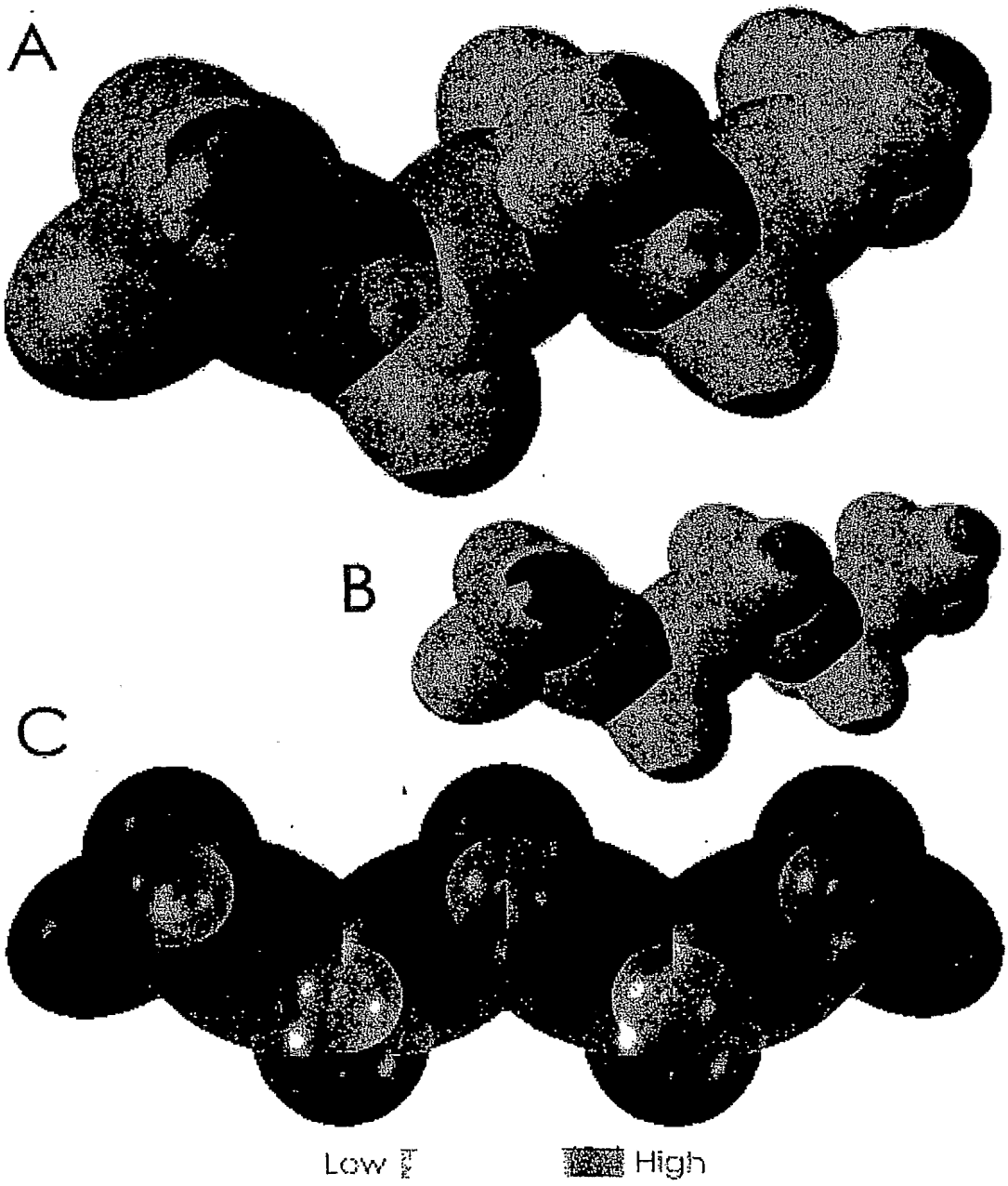


Fig.53

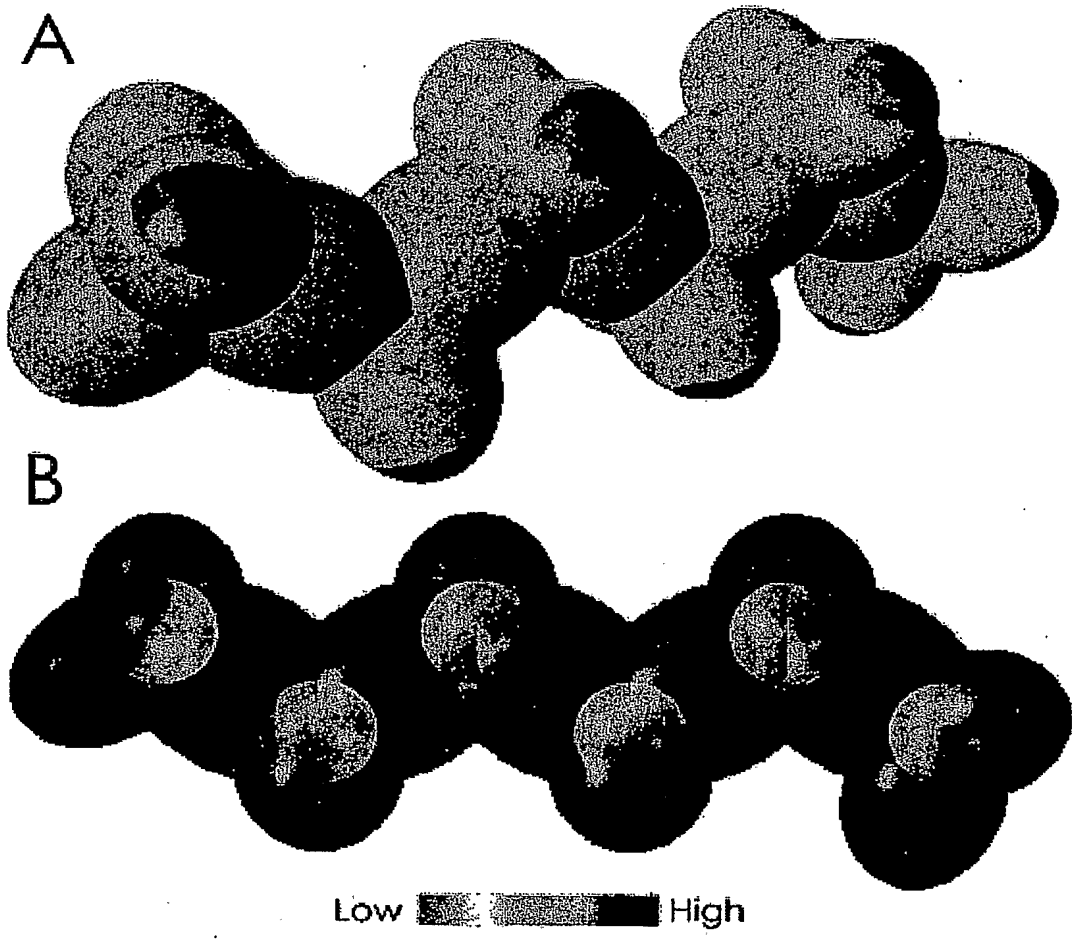


Fig.54

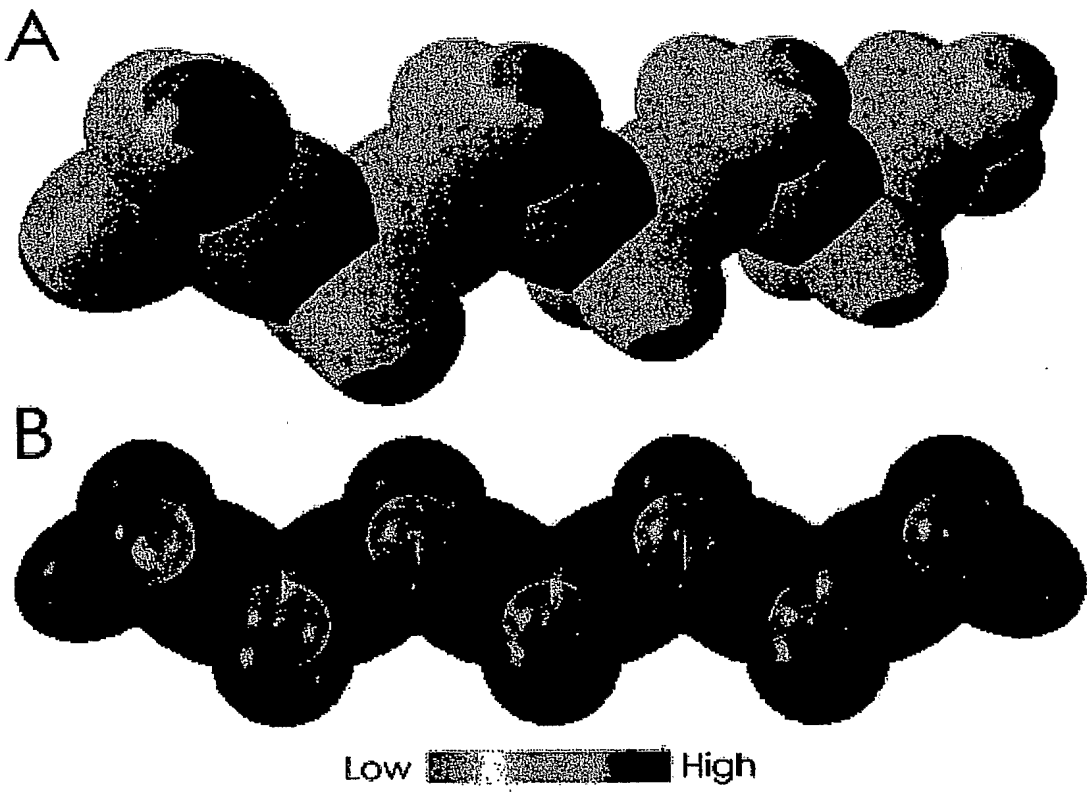


Fig.55

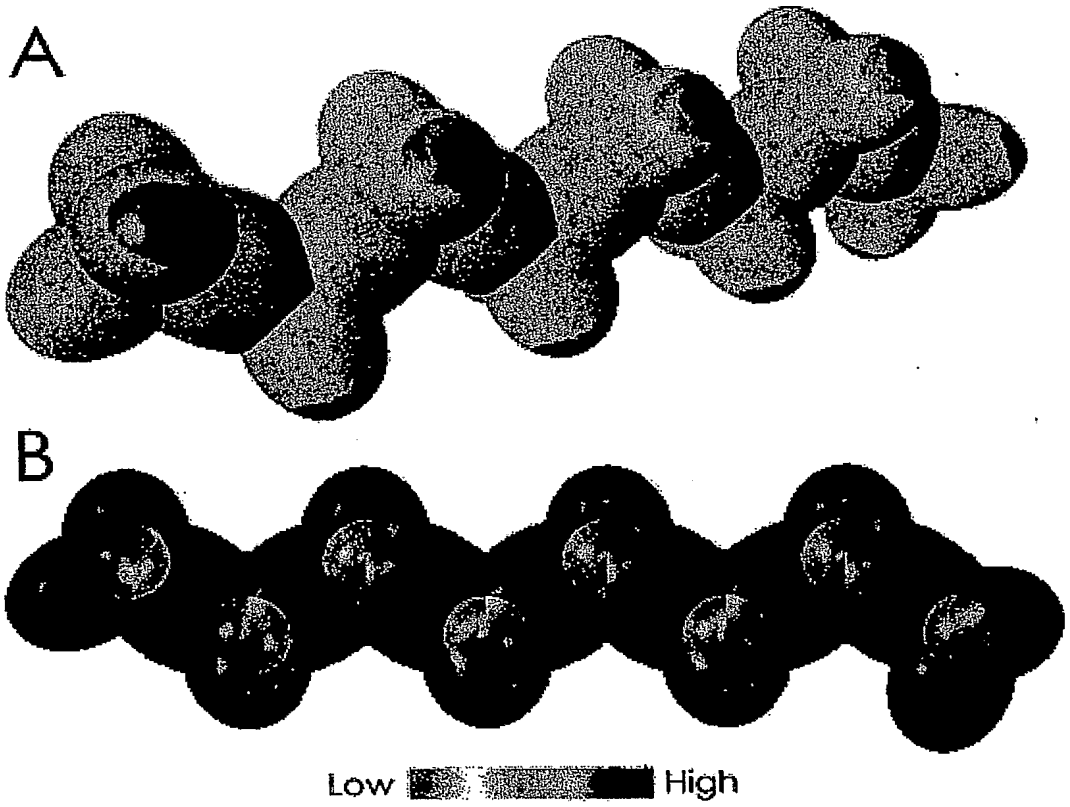


Fig.56

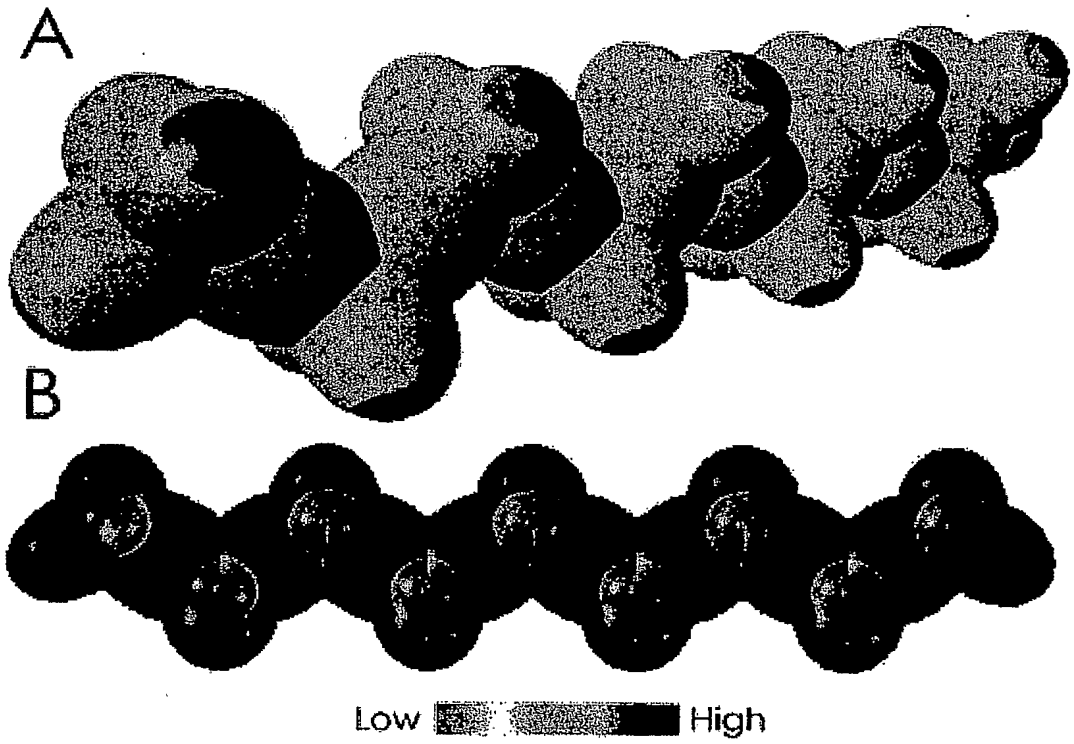


Fig.57

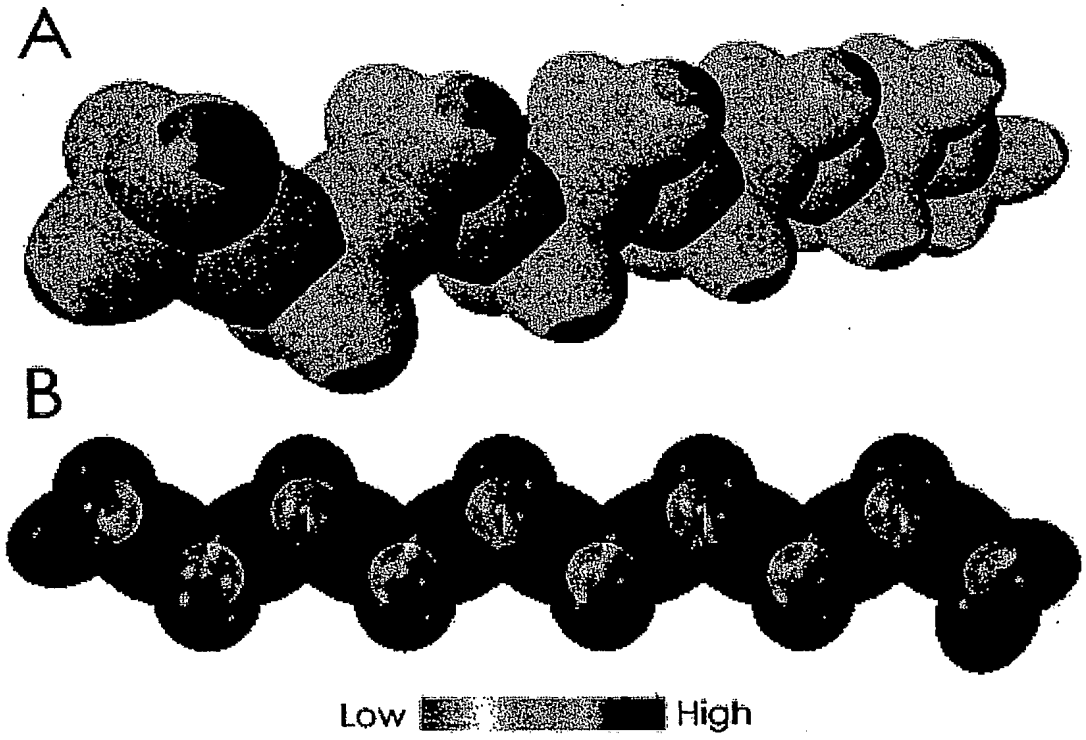


Fig.58

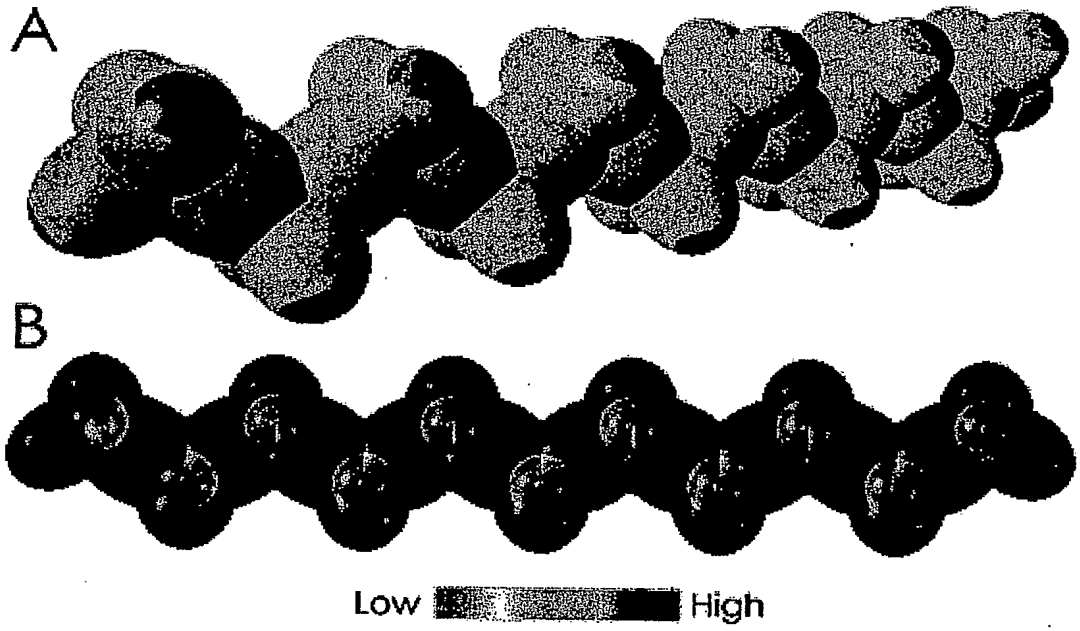


Fig.59

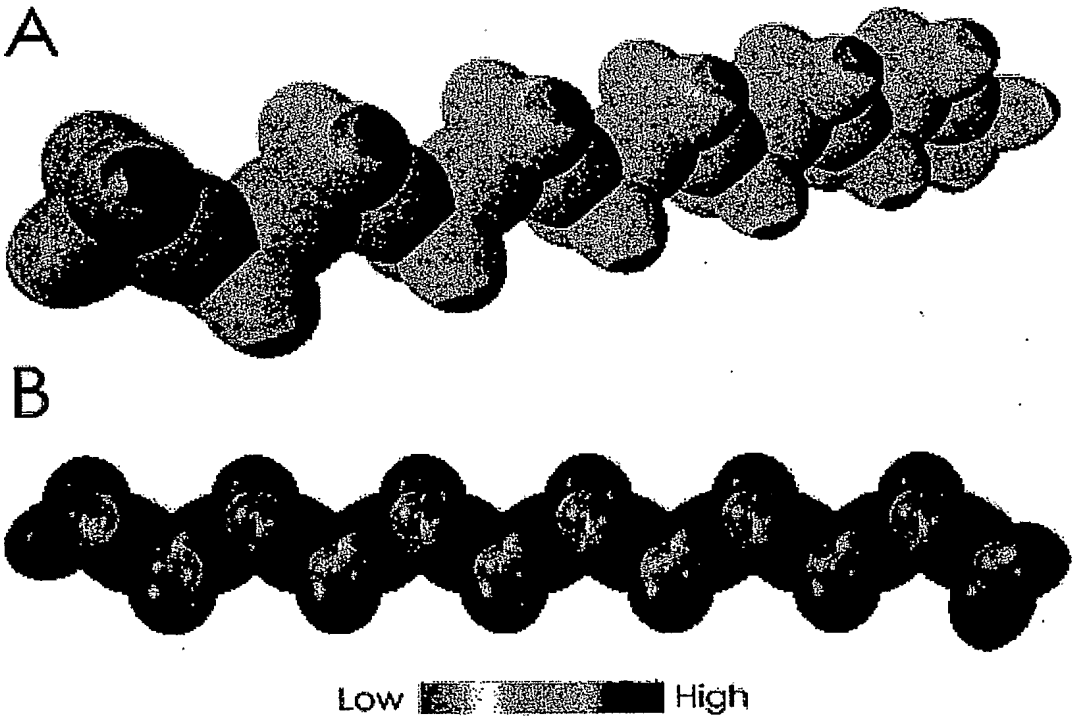


Fig.60

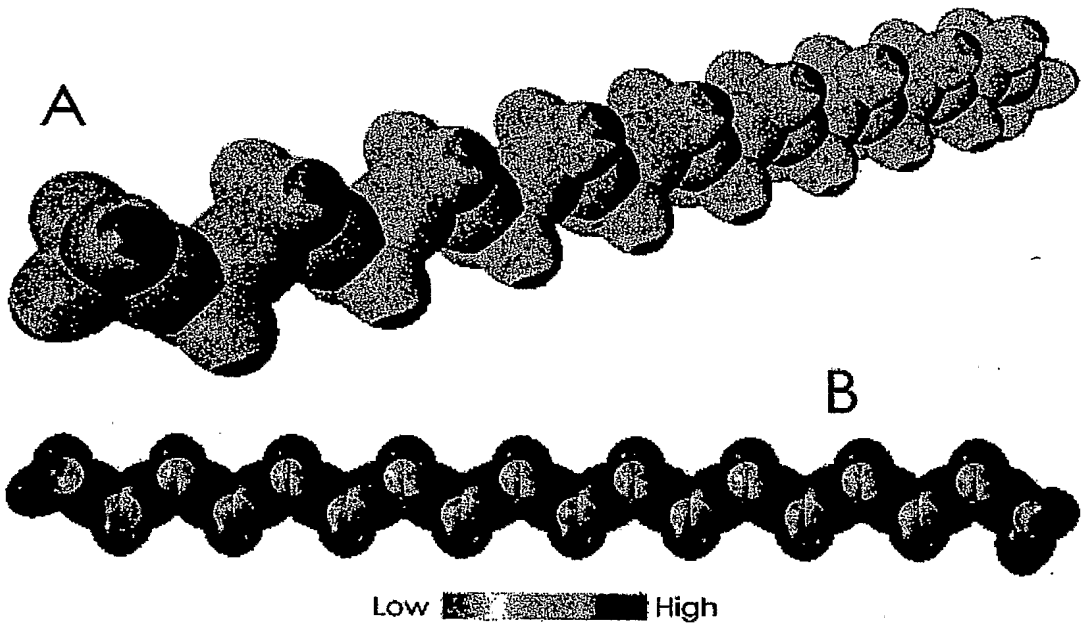


Fig. 61.A

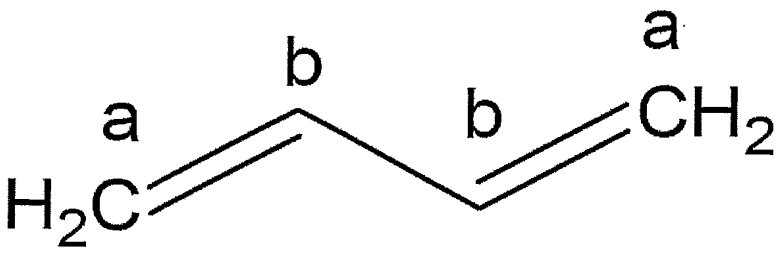


Fig. 61.B

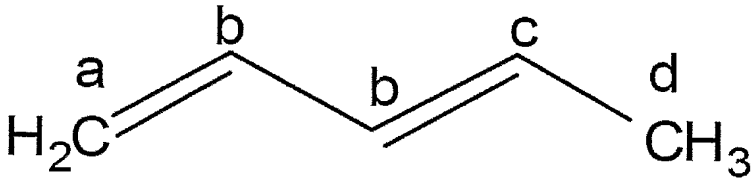


Fig. 61.C

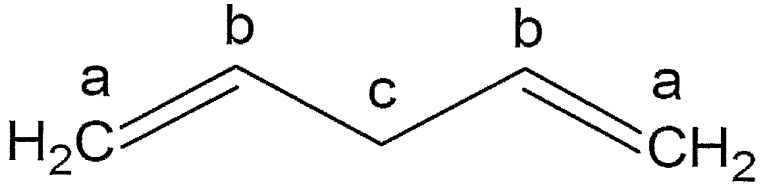


Fig. 61.D

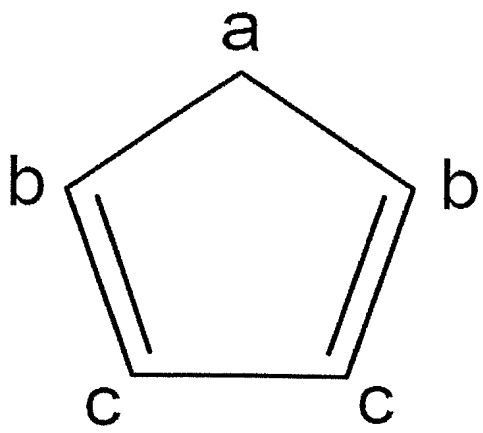


Fig. 61E

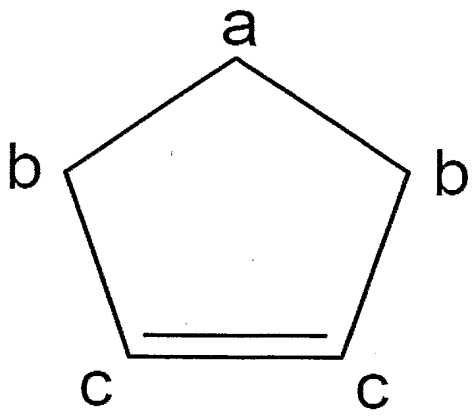


Fig. 62

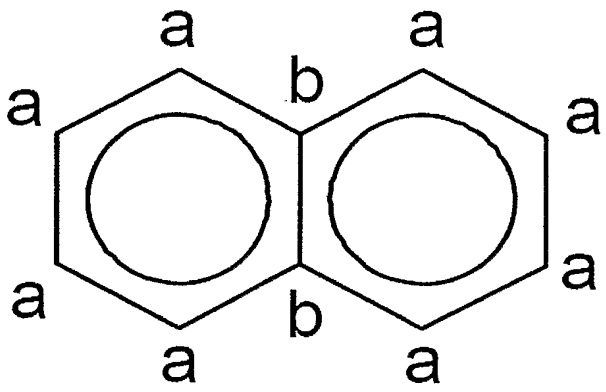


Fig. 63

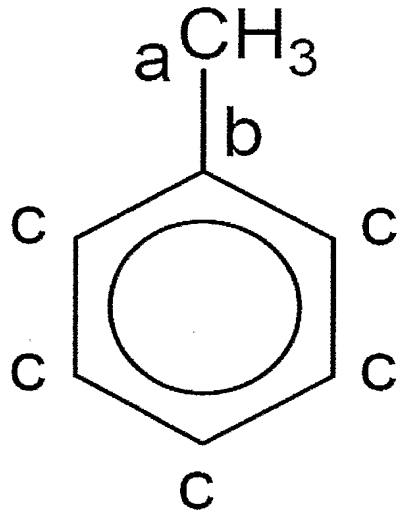


Fig. 64

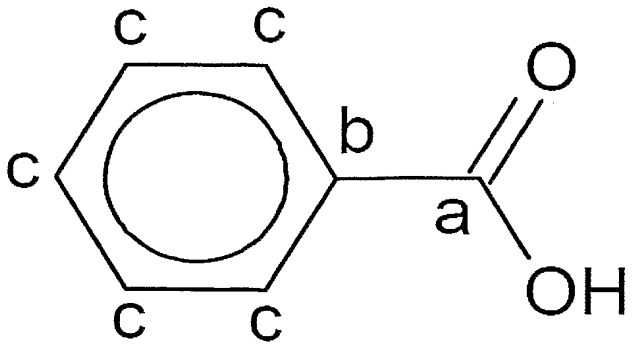


Fig. 65

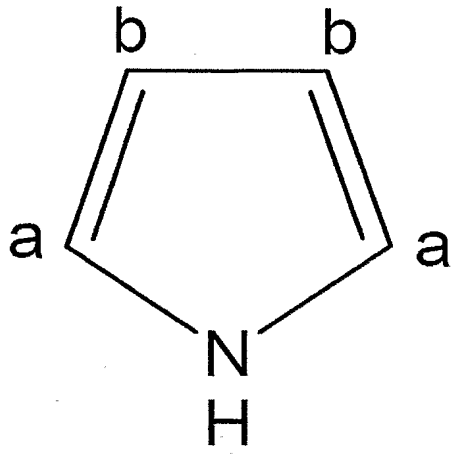


Fig. 66

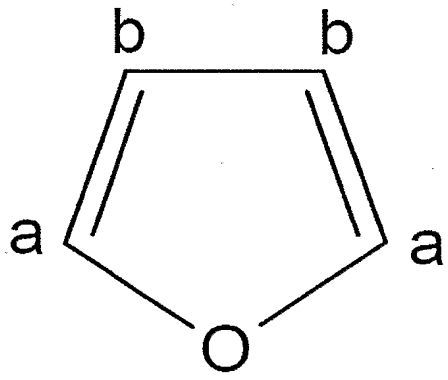


Fig. 67

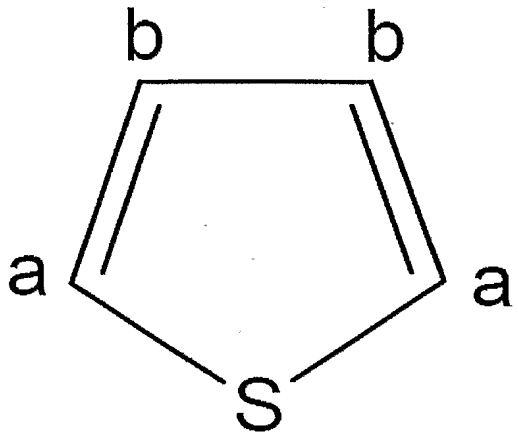


Fig. 68

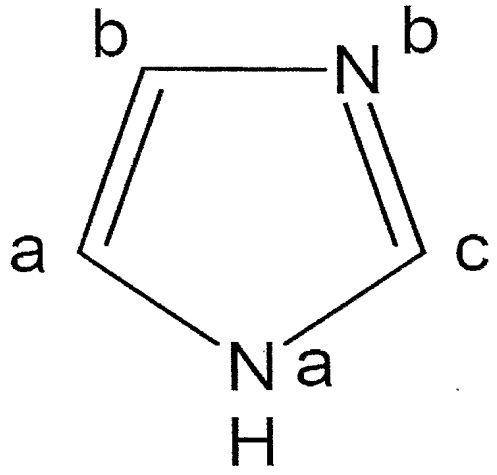


Fig. 69

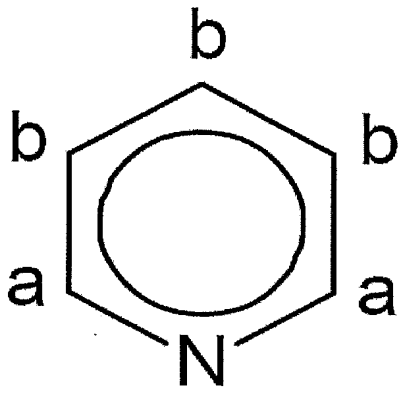


Fig. 70

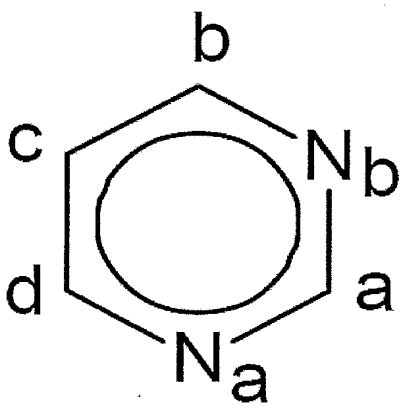


Fig. 71

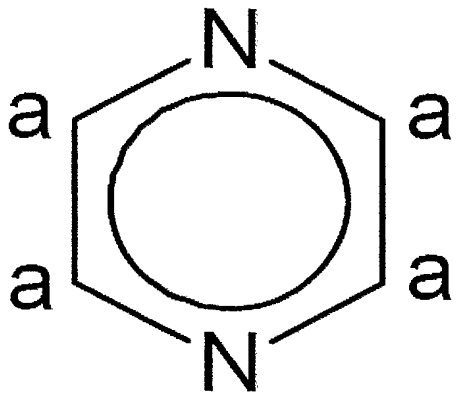


Fig.72

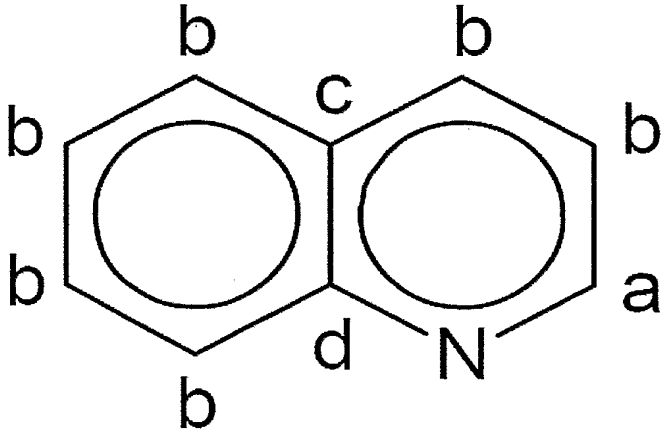


Fig. 73

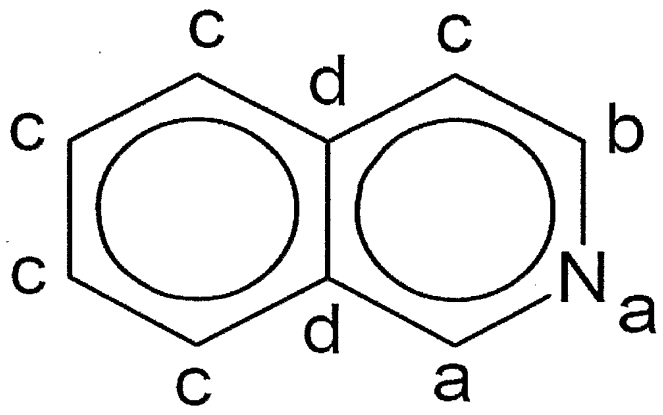


Fig. 74

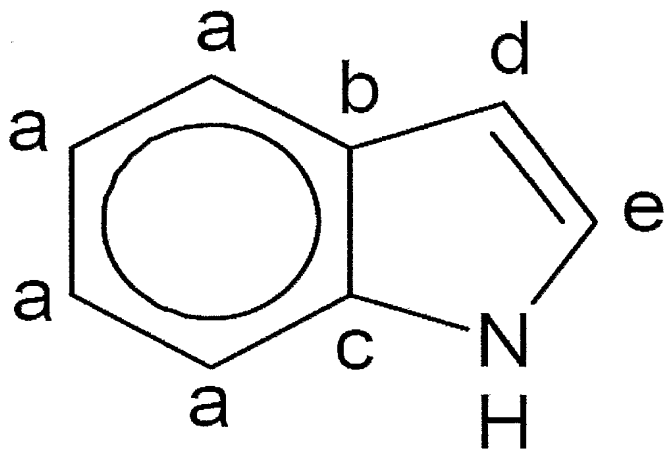
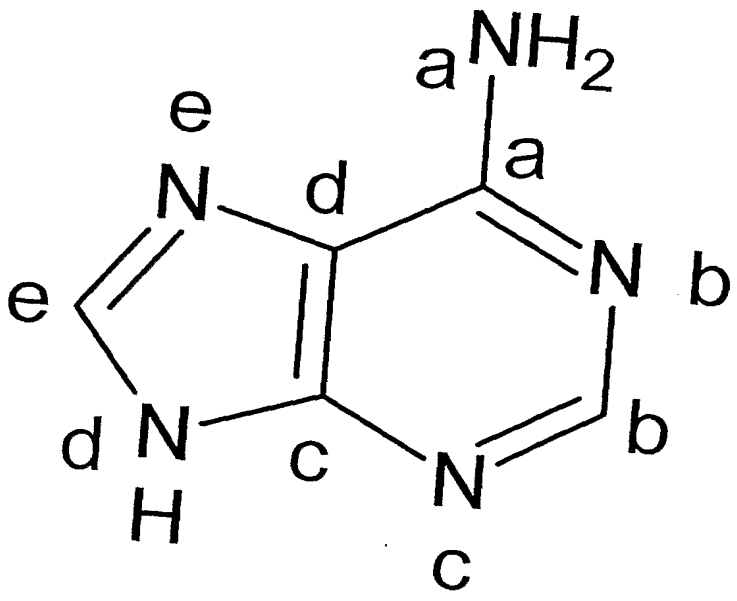


Fig. 75



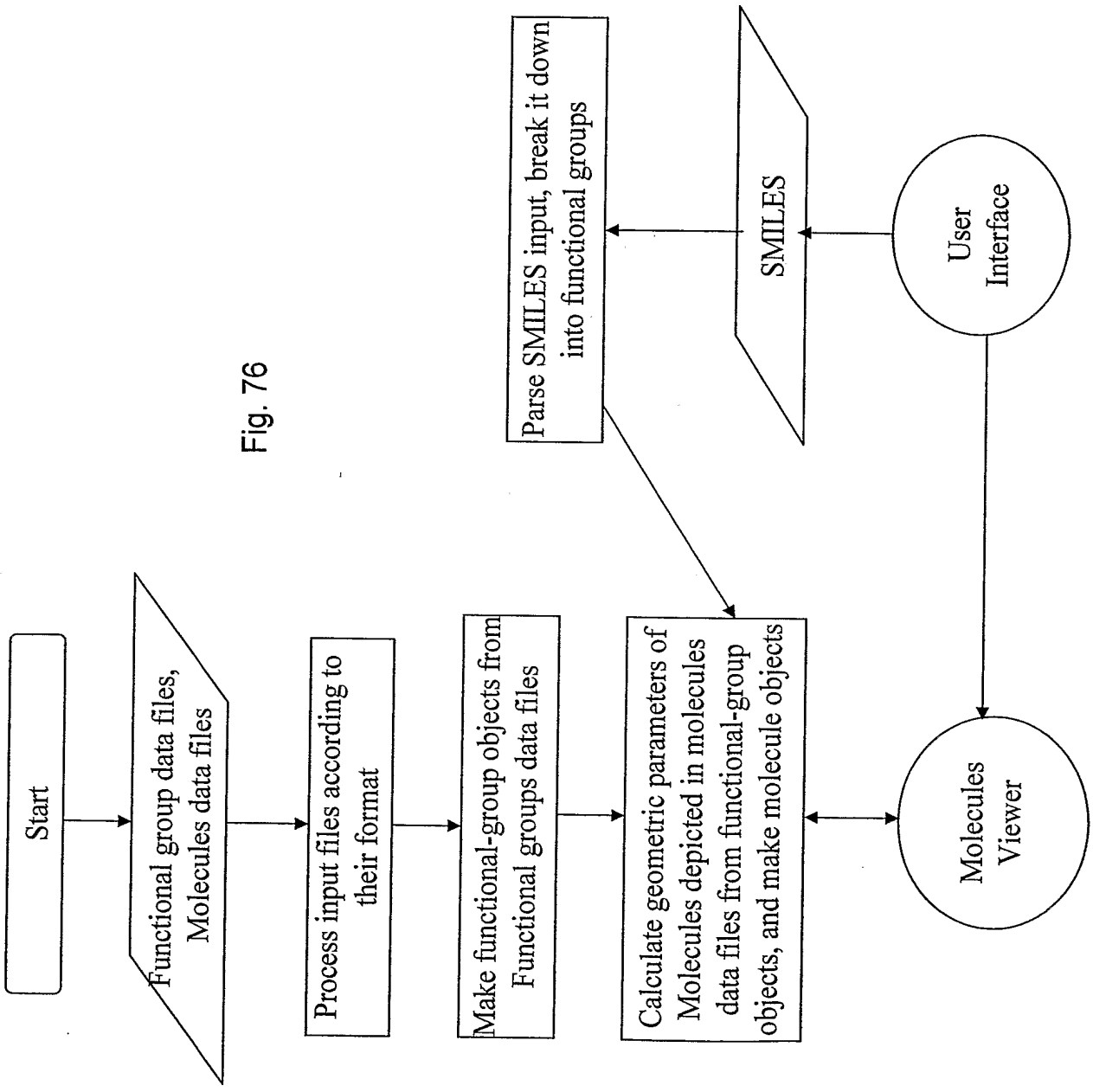

Start
Functional group data files, Molecules data files
Process input files according to their format
Make functional-group objects from Functional groups data files
Calculate geometric parameters of Molecules depicted in molecules data files from functional-group objects, and make molecule objects
Parse SMILES input, break it down into functional groups
SMILES
User Interface
Molecules Viewer

Fig. 76

Fig. 77

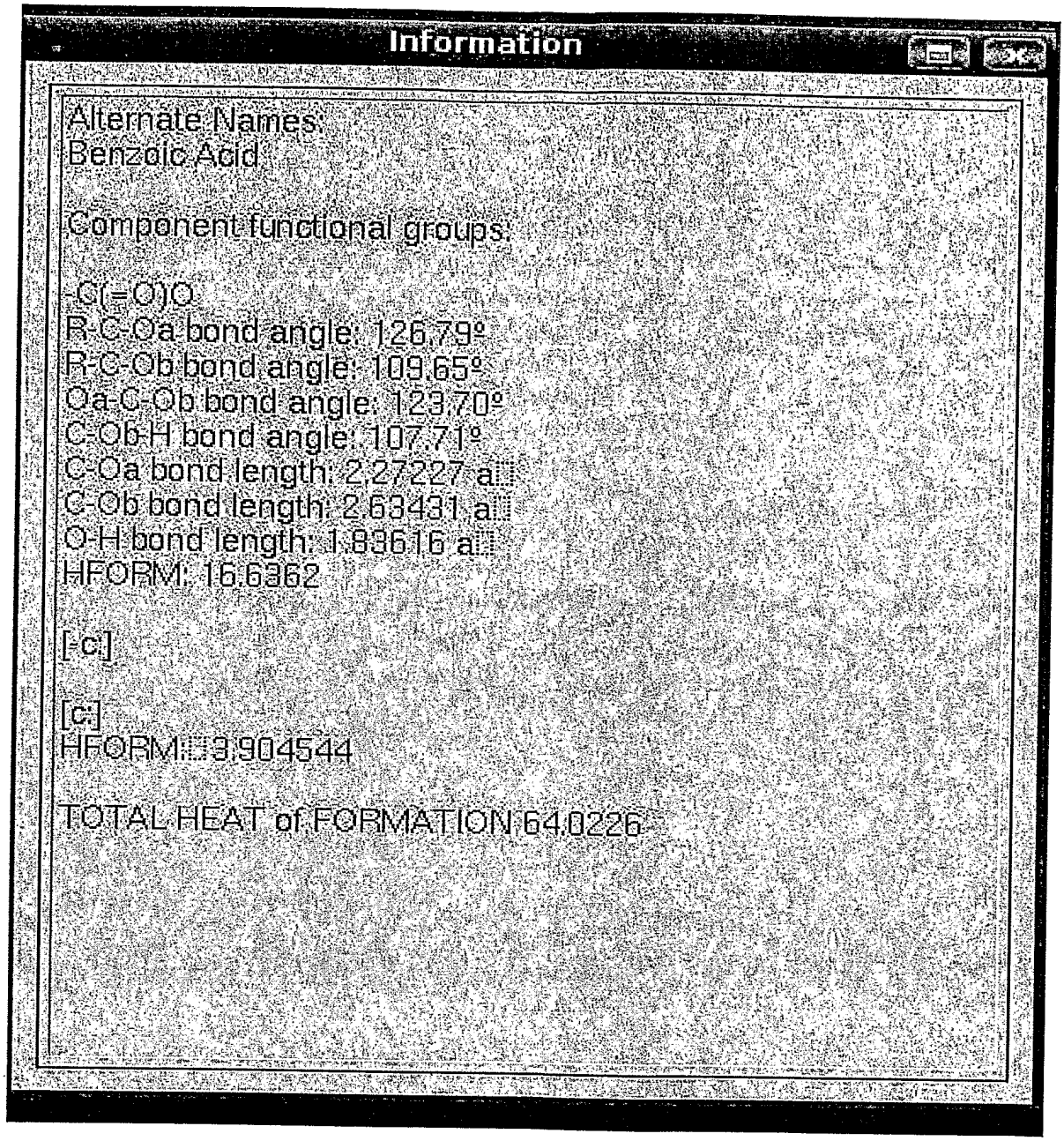
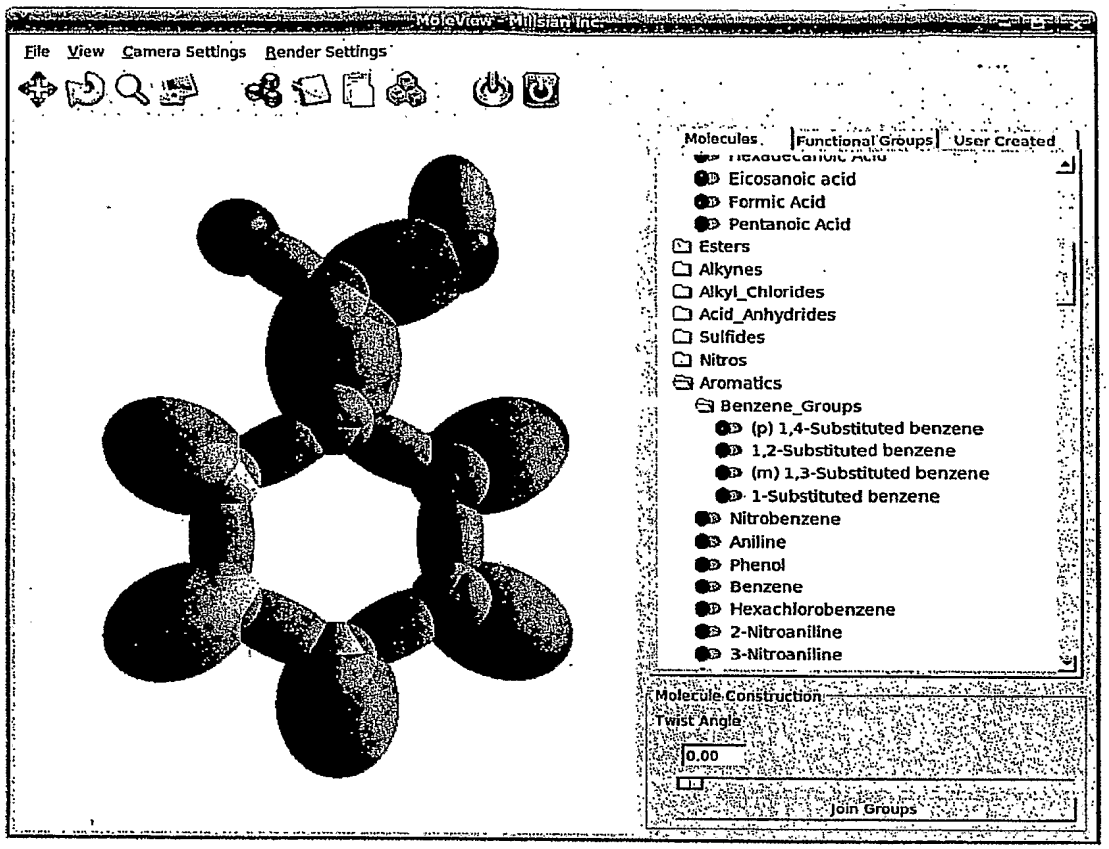

Information
Alternate Names:
Benzoic Acid
Component functional groups:
-C(=O)O
R-C-Oa bond angle: 126.79º
R-C-Ob bond angle: 109.65º
Oa-C-Ob bond angle: 123.70º
C-Ob-H bond angle: 107.71º
C-Oa bond length: 2.27227 a
C-Ob bond length: 2.63431 a
O-H bond length: 1.83616 a
HFORM: 16.6362
[-c]
[c:]
HFORM: 3.904544
TOTAL HEAT of FORMATION 64.0226

Fig.78


File View Camera Settings Render Settings
Molecules
Functional Groups
User Created
Eicosanoic acid
Formic Acid
Pentanoic Acid
Esters
Alkynes
Alkyl_Chlorides
Acid_Anhydrides
Sulfides
Nitros
Aromatics
Benzene_Groups
(p) 1,4-Substituted benzene
1,2-Substituted benzene
(m) 1,3-Substituted benzene
1-Substituted benzene
Nitrobenzene
Aniline
Phenol
Benzene
Hexachlorobenzene
2-Nitroaniline
3-Nitroaniline
Molecule Construction
Twist Angle
0.00
Join Groups